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Major Ions, Acid-Base and Dissolved Aluminum Chemistry of Selected Lakes in Mount Rainier National Park

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CA-9000-3-0003
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ABSTRACT

Sixteen lakes in Mount Rainier National Park were sampled between July 3 and September 27, 1985. All of the sampled lakes were analyzed for total dissolved, labile, and nonlabile aluminum; major anions; major cations; dissolved silica; dissolved organic carbon; and pH. The objectives of the study were to determine the sensitivity to and extent of acidification, and to provide seasonal variability information with respect to dissolved aluminum and acid-base chemistry of the sampled lakes.

Mount Rainier lakes are typically highly sensitive to acidification although any existing level of acidification is below the detection limits of the available models. Lake aluminum concentrations follow theoretical predictions, appear to be controlled by an aluminum trihydroxide solid phase similar to natural gibbsite, and do not indicate acidification Seasonal variation of aluminum is a result of variation in organically complexed aluminum concentration responding to variations in dissolved organic carbon.

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1.0 INTRODUCTION AND OBJECTIVES

The term "acid precipitation" has been used to describe precipitation that has a pH below 5.6, the pH of distilled water in equilibrium with atmospheric carbon dioxide (0.03% CO_2 at sea level) and that has elevated concentrations of sulfate, nitrate, or chloride (Henricksen, 1983). Acidic precipitation has been reported as a serious problem in the Northeastern United States, Southeastern Canada, and Scandanavia (Driscoll, 1980; Dillon et al., 1980; Henricksen, 1978). The increasing acidity of precipitation in Europe and North America has largely been attributed to an increase in sulfuric and nitric acid aerosols produced by metal smelting, industrial processes, and fossil fuel consumption. Released into the atmosphere, sulfur and nitrogen oxides react with water and oxygen to form sulfuric and nitric acid.

For an aquatic system, the effect of acidic deposition is dependent on the capacity of the soil and water to neutralize the acids and resist changes in pH. The carbonate system provides the dominant buffer capacity for water. Aluminum compounds play a significant role in soil neutralization. Previous work has shown acid precipitation to result in increased aluminum concentrations in the Northeastern United States and Scandanavia (Johnson et al., 1981).

Areas susceptible to acid precipitation generally have shallow soils, are underlain by unreactive bedrock, and have small drainage to lake surface area ratios. The Oregon and Washington Cascade Mountain lakes are classified among the most sensitive in the United States (Omernik and Powers, 1982). Due to their sensitive nature Cascade lakes would be expected to respond quickly to low levels of acidification.

Acid precipitation has been reported for the Central and North Cascades of Washington State with low level acidification reported for dilute lakes in the Alpine Wilderness Area of the Central Washington Cascades (Welch et al., 1985). Preliminary investigations by the United States Geological Survey (U.S.G.S., 1986) in terms of potential lake acidification in Mount Rainier National Park suggested early stages of acidification in some lakes because of elevated levels of aluminum.

The increased acidity of Washington's precipitation appears to be due to an increase in sulfuric acid aerosols. The primary source for anthropogenic sulfur in Washington State is the Centralia Power Plant (59,000 tons/year) (Logan et al., 1982). The ASARCO smelter near Tacoma, which closed in 1985, had been releasing 80,000 tons/year. A significant amount of the acidity in rainfall may also be derived from nitrogen oxides contributed to the atmosphere by internal combustion engines in the urbanized Southern Puget Sound lowlands around Seattle and Tacoma (Welch and Chamberlain, 1981). Prevailing southwest winds carry these atmospheric constituents into the Cascades. With respect to the lakes in Mount Rainier National Park, the objectives of this study were to:

1) Characterize the major ion and aluminum chemistry, building on the data base of the U.S.G.S.,
2) Provide seasonal variability information on water chemistry data,
3) Determine sensitivity to, or extent of acidification, with respect to major ion and aluminum chemistry.

2.0 THEORETICAL BACKGROUND

The acidification process may be described as a titration of a bicarbonate dominated solution with a strong acid. Because of their prevalence in anthropogenic emissions, sulfate molar concentrations ($[SO_4^{2-}]$) or sulfate plus nitrate molar concentrations ($[SO_4^{2-}] + [NO_3^-]$) are often used as surrogates for the strong acid. During the initial stages of the acid titration, bicarbonate formed through weathering will consume the acid and thereby buffer the system against changes in pH. During this phase it is difficult to detect acidification from changing pH because of the masking effect of the bicarbonate buffering and the natural pH fluctuations induced by temporal variations of p_{CO_2}. Only when the bicarbonate buffering is nearly exhausted does pH variation due to acidification occur.

Alkalinity is a capacity measurement, unlike pH which is an intensity measurement, and is unaffected by variation in p_{CO_2}. Having greater natural stability and being initially more responsive than pH, alkalinity provides a more suitable parameter for detecting acidification. The amount of acidification is relative to the alkalinity consumed by the acid titration. Acidification therefore is estimated by the difference between preacidification alkalinity and present alkalinity. An accurate measurement of original alkalinity is usually not available and must be empirically estimated from contemporary water quality data.

Chemical acidification models, used to estimate original alkalinity, are based on the concept of geochemical weathering. Inherent assumptions in the empirical models include: 1) electroneutrality or ionic balance requires that a solution must have a neutral charge; 2) there is no nonatmospheric (indigenous) source of chloride in the watershed; 3) carbonic acid

weathering, which produces equivalent amounts of bicarbonate alkalinity ($[HCO_3^-]$) and cations, dominates the system; and 4) cation concentrations remain constant at low levels of acidification.

2.1 Electroneutrality

To satisfy the law of electroneutrality, the equivalent concentration of positively charged ions must equal the equivalent concentration of negatively charged ions in aqueous solution. The electroneutrality equation and carbonate equilibrium equations provide the foundation for theoretical and empirically derived models of acidification. The suitability of a model for determining acidification is dependent on the applicability of the assumptions made in the theoretical equations and empirical simplifications. The derivations of theoretical and empirical acidification models are presented in Table 1.

Table 1

Derivation of Theoretical and Empirical
Acidification Models

Electroneutrality:

1. $[H^+]+[NH_4^+]+2[Ca^{2+}]+2[Mg^{2+}]+[Na^+]+[K^+] =$

$[HCO_3^-]+2[SO_4^{2-}]+[Cl^-]+[NO^-_3]+[OH\_]$

Assume: No $[Cl^-]$ input from watershed (sea salt correction), $[NO_3^-]$ and $[NH_4^+]$ concentrations are negligible, and pH < 7:

2. $[H^+]+2[Ca^{2+}]+2[Mg^{2+}]+[Na^+]+[K^+] = [HCO_3^-]+2[SO_4^{2-}]$

By defining Σ [cations] as Σ $([M_i]z_i)$ where M_i represents the metal cation and z_i represents the ionic charge:

3. $[H^+]+ \Sigma\,[\text{cations}] = [HCO_3^-]+2[SO_4^{2-}]$

Alkalinity Definition:

4. $[\text{Alkalinity}] = [HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+]$

Simplified at pH < 7:

5. $[\text{Alkalinity}] = [HCO_3^-]-[H^+]$

Substituting above expression (eq. 5) into the simplified charge balance equation (eq 3):

6. $[\text{Alkalinity}] = \Sigma\,[\text{cations}]-2[SO_4^{2-}]$

For predicting original alkalinity, assume:

Natural (Background) $[SO_4^{2-}]$ is negligible.

7. $[\text{Alkalinity}] = \Sigma\,[\text{cations}]$

Substituting empirical correlations for Σ [cations]:

8. $b\,([Ca^{2+}]+[Mg^{2+}]) = \Sigma[\text{cations}]$, and:

9. $b'\,([Ca^{2+}]) = \Sigma[\text{cations}]$; where b and b' are constants. Substituting above equations 8 and 9 into equation 7:

10. $[\text{Alkalinity}] = b([Ca^{2+}]+[Mg^{2+}])$

11. $[\text{Alkalinity}] = b'([Ca^{2+}])$

Carbonate Equilibrium:

12. $CO_2(g) + H_2O = {}^*H_2CO_3$; K_H, where K_H is Henry's constant, and:

13. $H_2CO_3 = HCO_3^- + H^+$; Ka_1, where Ka_1 is the first carbonic acid dissociation constant.

Genesis of alkalinity and cations from congruent dissolution:

14. $MCO_3(s) + H^+ = M^{2+} + HCO_3^-$; where M = mineral (metal cation). By combining equations 12, 13 and 14:

15. $MCO_3(s) + CO_2(g) = M^{2+} + 2HCO_3^-$

By combining equations 12 and 13, and defining ${}^*K_1 = K_H\, K_{a1}$:

16. ${}^*K_1 = [HCO_3^-][H^+]/p_{CO_2}$

Substituting from eq. 7 into ${}^*K_1$ equation:

17. ${}^*K_1 = \Sigma\,[\text{cations}][H^+]/p_{CO_2}$

Taking logarithms:

18. $pH = \log \Sigma\,[\text{cations}] - \log {}^*K_1 - \log\, p_{CO_2}$

Or, substituting from empirical equation 9:

19. $pH = \log(b'[Ca^{2+}]) - \log {}^*K_1 - \log\, p_{CO_2}$

Letting $\alpha = \log b' - \log {}^*K_1 - \log\, p_{CO_2}$:

20. $pH = \alpha + \log\, [Ca^{2+}]$

Sea salt corrections of lake water ionic composition are based on assumption two, that no indigenous sources of chloride exist in the watershed. Thus the chloride present is assumed to be derived from sea salts. It is further assumed that the ion ratios of sea salt and sea spray relative to chloride are the same. To maintain electroneutrality, both cation and anion concentrations are corrected for sea salt contributions relative to chloride. The assumption that the ratio of each ion in sea salt or natural wet deposition is invariant relative to chloride concentration, however, is not strictly correct. Both potassium and calcium are associated with terrestrial dusts (Gorham and Martin, 1984; and Deither, 1979). The effect of terrestrial dusts is usually minor compared to total ionic concentrations (Wright and Gjessing, 1976).

2.2 Empirical Models

Surface water acidification is estimated by comparison of measured data with the theoretical and empirical models presented in Table 1. Equations 1-7 are rigorous if the assumptions inherent in their derivations are verified. Equations 8-12 involve empirical simplification but may be applied over limited conditions where relative ratios of cations and anions do not vary drastically. Alternatively, substitution of carbonate equilibria (weak acid and solid dissociation reaction) into the electroneutrality - based equations leads to pH vs. cation concentration equations (e.g. 17-20, Table 1).

Graphical presentation of water chemistry data facilitates comparison with theoretical or empirical models and can be used to estimate acidification. The electroneutrality equation applied to lakes dominated

by carbonic acid weathering results in a linear equivalence between bicarbonate and total cation concentrations, i.e., slope = 1 and y-intercept = 0 (eq. 7, Table 1). A slope lower than unity indicates input of cations from mechanisms other than carbonic acid weathering or loss of alkalinity and is interpreted as evidence of acidification. The error in the y-intercept term is usually negative, and may be used to indicate the concentration of ions assumed negligible in the model formulation (Kramer and Tessier, 1982).

Empirical simplification of the electroneutrality equation leads to: $[\text{Alkalinity}]=b([Ca^{2+}]+[Mg^{2+}])$ and $[\text{Alkalinity}]=b'[Ca^{2+}]$ equations (Table 1). The multiplier (b and b') terms are greater than unity to account for the contribution of neglected cations. Variability in b or b' is introduced by differences in cation concentrations between watersheds and by possible acidification.

A rigorous approach for constructing a pH vs. cation diagram would be to use equation 18 (Table 1) to represent carbonic acid weathering since this equation is theoretically derived. To reduce error associated with p_{CO_2} variation the theoretical line representing carbonic acid weathering is drawn for a fixed p_{CO_2} and the pH measurement of the water to be plotted should be measured at that p_{CO_2} or be corrected for variation in pCO_2 using theoretical equilibrium equations. Any point falling above the theoretical equilibrium line indicates that sources of hydrogen ions other than carbonic acid are contributing to the weathering process. Henricksen, (1980) and Kramer and Tessier (1984) applied the empirically simplified charge balance equation between alkalinity and calcium (eq. 11, Table 1) to obtain the pH vs. $[Ca^{2+}]$ plot using the equation, $pH = \alpha - \log [Ca^{2+}]$ (eq. 20 Table 1). High variability is

introduced into the constant α by its component parameters b, p_{CO_2} and to a lesser extent by the composite dissociation constant *K for carbonic acid (Table 1). The empirical constant, b, varies significantly between surface waters. The p_{CO_2} may vary by one order of magnitude from one location to another or at the same location with time (Stumm and Morgan, 1981). *K is affected by both temperature and ionic strength. Despite the simplifying assumptions, pH vs. ion concentration plots are often employed to determine the relative acidification among lakes since many surface waters can be positioned on the same graph for comparison.

Assumption four, that cation concentrations remain stable with increasing acidification, has been questioned. Low level acidic deposition increases weathering reaction rates and can leach cations rather than titrating bicarbonate (Galloway et al., 1983). This obscures the titration effect and is prevalent in groundwater dominated systems (Henricksen, 1980). The titration concept appears most directly applicable to watersheds overlying unreactive bedrock characterized by shallow underflows and short retention times.

2.3 Aluminum Chemistry

When primary buffering systems are exhausted and pH declines from between 6-7 to below 5, the buffering system consisting of aluminum hydrolysis compounds becomes dominant (Driscoll et al., 1980). At pH values below 5, mineral dissolution reactions increase free and total aluminum concentrations.

Sensitive watersheds are generally underlaid by bedrock that has small pools of readily exchangeable (weatherable) basic cations and an

inability to retain acidic anions, such as SO_4^{2-}. Therefore, if high loadings of acid are not attenuated in the soil, but are instead removed by drainage water, the anionic solute must be accompanied by an equivalent charge of cations to maintain electroneutrality. It is supposed that, in the absence of readily available cation pools, soil neutralization will be incomplete and that dissolved labile monomeric aluminum will be transported from the soil to partially counter-balance the anionic solutes (Driscoll, 1985).

The ion exchange capacity of the soil appears to be seasonally responsive and may exert greater control over concentrations of aluminum than solubility reactions would predict (Klock and LeFohn, 1985). Differences among lakes in sensitivity and water chemistry are largely the result of variations in water flow through soil horizons and in the contact of the water with surficial geology.

There are several mitigating complexation reactions that limit the applicability of attributing elevated total aluminum concentrations to acidification. Aluminum forms complexes with sulfate, fluoride, organic carbon compounds, and hydroxide ions. These complexes may be significant in concentration thereby increasing total aluminum solubility independent of the rate of acid loading. Table 2 summarizes the aluminum chemical equilibria and corresponding thermodynamic data applied in this study.

Table 2

Thermodynamic equilibrium equations
used in this study (Driscoll, 1984)

Reaction	Equilibrium Constant
Hydroxide Ligands	
$Al^{3+}+H_2O = Al(OH)^{2+}+H^+$	$1.03x10^{-5}$
$Al^{3+}+2H_2O = Al(OH)_2^{+}+2H^+$	$9.36x10^{-11}$
$Al^{3+}+4H_2O = Al(OH_4)^{-}+4H^+$	$6.93x10^{-23}$
Aluminum Trihydroxide	
$Al(OH)_3(s)+3H^+ = Al^{3+}+3H_2O$	
Synthetic Gibbsite	$1.29x10^{8}$
Natural Gibbsite	$5.89x10^{8}$
Microcrystalline Gibbsite	$2.24x10^{9}$
Fluoride Ligands	
$Al^{3+}+F^- = AlF^{2+}$	$1.05x10^{7}$
$Al^{3+}+2F^- = AlF_2^{+}$	$5.77x10^{12}$
$Al^{3+}+3F^- = AlF_3$	$1.07x10^{17}$
$Al^{3+}+4F^- = AlF_4^{1-}$	$5.37x10^{19}$
$Al^{3+}+5F^- = AlF_5^{2-}$	$8.33x10^{20}$
$Al^{3+}+6F^- = AlF_6^{3-}$	$7.49x10^{20}$
Sulfate Ligands	
$Al^{3+}+SO_4^{2-} = AlSO_4^{+}$	$1.63x10^{3}$
$Al^{3+}+2SO_4^{2-} = Al(SO_4)_2^{-}$	$1.29x10^{5}$

3.0 METHODS AND PROCEDURES

3.1 Study Area

All lakes studied are in Mount Rainier National Park, Washington, located 56 km (35mi) southeast of Tacoma. Mount Rainier Park covers 979 Km^2 (378 mi^2) surrounding the 4,392 m (14,410 ft) peak. Annual precipitation is high, 151 to 254 cm (60 to 100 in), much of it falling as snow at this high elevation. The park has numerous lakes with small drainage basins characterized by shallow soils and weathering resistant bedrocks.

Lakes of various morphologies were sampled from all sides of Mount Rainier, with elevations ranging from 1,200 to over 2,000 m (4000 to 6800 ft) as shown in Figure 1. Drainages varied in size, forest type, and forest age. Most lakes could be characterized as shallow, (< 16 m) with small surface area/watershed ratios, low productivities and short water residence times. These lake characteristics are indicative of sensitive lakes (Driscoll, 1985; Galloway et al., 1983; and Henricksen, 1980). Based on a previous study (U.S.G.S., 1986) six key lakes were identified, three of which had high total aluminum concentrations (Golden, Unnamed, and Shriner), and were matched by drainage type to three lakes which had low total aluminum concentrations (Mowich, Crystal, and Allen). Ten other lakes were selected to provide a spectrum of drainage and lake characteristics. Table 3 summarizes the physical characteristics of the study lakes.

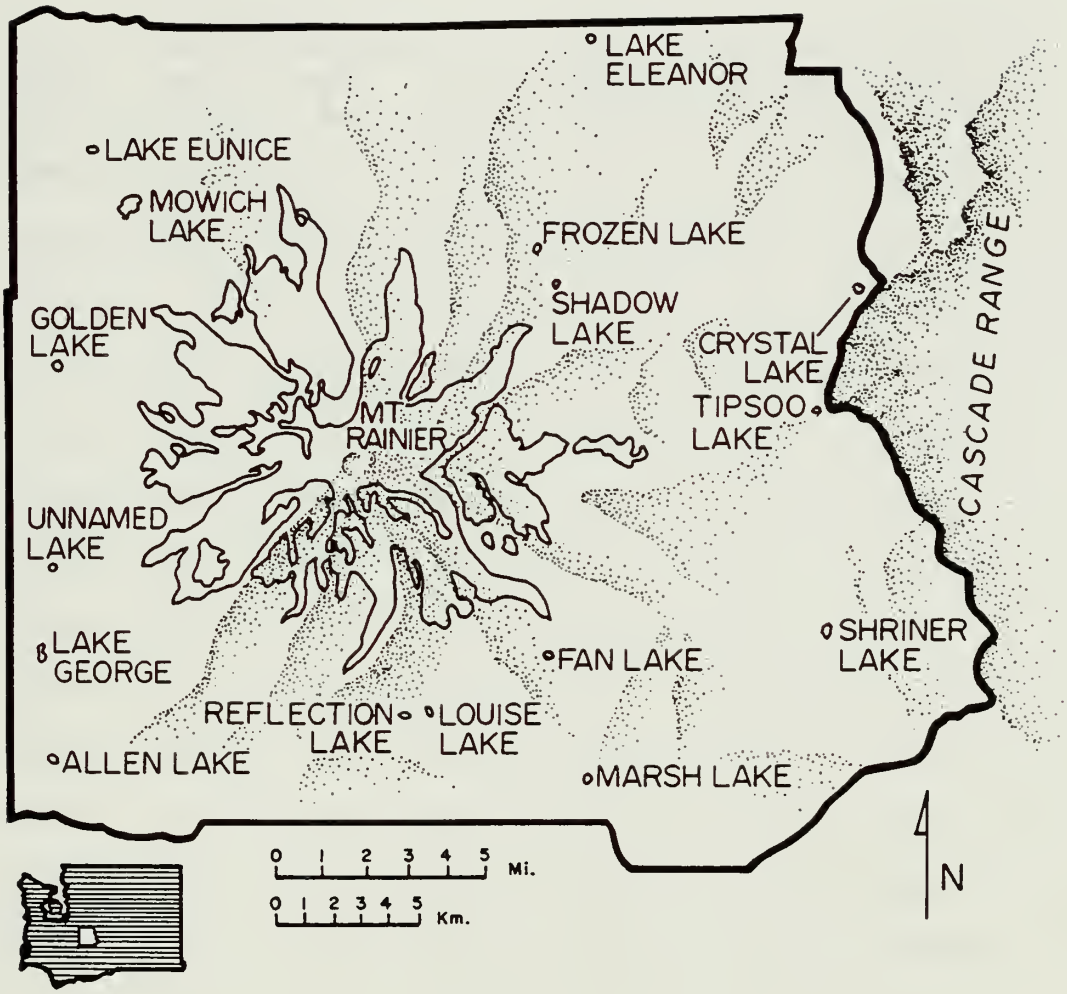


Figure 1. Study Lakes Mount Rainier National Park

TABLE 3

Physical Characteristics of the Lakes Studied

Lake	Altitude m	Max. Depth m	Sampling Depth m	Area ha	Inflow Observed	Outflow Observed	Relative Vegetation Density
Golden	1389	6.1_r	24.1	7.3	Y	Y	thick
Unnamed	1379	3.7_r	11.43	0.8	N	Y	thick
Shriner	1306	6.1_e	2.8	3.6	I	Y	thin
Crystal	1777	22.9_r	9.4	3.6	I	I	moderate
Allen	1410	7.6_e	7.6	2.0	N	I	moderate
Mowich	1289	59_m	30.5	49.6	Y	Y	moderate
Louise	1400	18.3_e	17.4	6.9	Y	Y	moderate
Shadow	1890	4.6_e	4.9	1.2	N	Y	thin
George	1290	45.7_r	30.5	13.3	N	N	moderate
Marsh	1204	6.1_e	3.2	1.6	N	Y	thick
Tipsoo	1620	4.6_r	2.4	2.6	N	Y	thin
Frozen	2057	5.5_r	6.1	1.01	N	Y	thin
Eunice	1632	sh	19.2	4.9	N	Y	moderate
Reflection	1482	18.2_r	10.1	5.3	N	Y	thin
Eleanor	1512	12.2_e	12.8	7.9	N	Y	moderate
Fan	1648	sh	0.5	2.0	N	Y	thin

r = reported, unverified

e = estimated

m = measured

sh = shallow

I = intermittent, July sampling trip only

Y = yes

N = no

3.2 Field Sampling

3.2.1 Data Collection

The key lakes were sampled three times each between July 3 and September 27, 1985. The ten other lakes were sampled one time each during the same period.

Water samples were collected and stored in 1 liter (1.06 qt) polyethylene bottles. Prior to collection, the sample bottles were washed with 1 N nitric acid, thoroughly rinsed with deionized water, and final-rinsed on site with water from the lake to be sampled. Samples were stored on ice within three hours of collection and subsequently refrigerated at 4^{O}C in the lab trailer and home lab until analysis.

Water samples were collected at two depths for the fifteen spatially sampled lakes using a 2 liter (2.15 qt) Van Dorn bottle water sampler. Two 1 liter (1.06 qt) "surface" samples were collected 1 meter (3.3 ft) below the surface. A 1 liter (1.06 qt) "depth" sample was collected 1 meter (3.3 ft) above the lake bottom or at 30.5 m (100 ft), whichever was less. Samples were obtained from the region of maximum depth as determined by a weighted and calibrated drop line. In-situ pH was determined from a subsample of the collected water sample.

Temperature and dissolved oxygen (DO) profiles were determined from all spatially sampled lakes at 0.76m (2.5 ft) or 1.5m (5 ft) intervals to a maximum depth of 15.24 meters (50 ft) using a polarographic oxygen meter (Y.S.I. Model 54) (Y.S.I., 1980). Prior to sampling, the instrument was calibrated on site for altitude (as determined from U.S.G.S. quadrangle maps) and for ambient temperature. Equilibration time for DO and temperature readings was three to five minutes or greater.

All samples at Fan Lake and the August sample at Tipsoo lake were grab sampled from the shore at a depth of 0.5m. Sampling location was near the lake outlet and was selected to avoid areas where the physical characteristics differed from those of the general littoral zone. Temperature and in-situ pH data were also collected at the sampling location.

All in-situ pH measurements were made with a portable digital pH meter (Orion Model 211) and a combination electrode (Orion Model 91-05). The pH meter was standardized on site at pH 7 and the slope was calibrated at pH 4 (Orion, 1981). To avoid temperature induced error, the pH of the buffers and samples was determined at their respective temperatures. To limit the error induced by CO_2 exchange between sample water and the atmosphere a narrow necked 125 ml plastic bottle was used for in-situ pH measurement. Field pH was determined immediately upon retrieving the sample. The pH and temperature equilibration time varied from five to fifteen minutes.

3.2.2 Lab Trailer

A mobile laboratory trailer provided facilities in the field for equipment preparation, instrument calibration, and initial sample processing and storage. Aluminum samples were fractionated into labile and non-labile (organically complexed) components and fixed for later analysis.

3.3 Laboratory Analyses

All water samples collected were measured for laboratory equilibrated pH, conductivity, alkalinity, major metal cations (calcium, magnesium, sodium, potassium), fluoride, total aluminum, chloride, sulfate, total dissolved organic carbon (DOC) and dissolved silica. In addition, organically complexed aluminum was determined for surface samples.

3.3.1 Laboratory pH

Lab equilibrated pH was determined in conjunction with alkalinity titrations. Three digital pH meters (Orion Model 601-A) with combination electrodes (Model 91-05) were used (Orion. 1977A). To ensure consistency, results were verified using a single pH meter with a Ross combination electrode (Orion Model 81-02). The pH meters were calibrated at pH 7, and the slope was adjusted at pH 4 at ambient temperature immediately before use and between each sample measurement. Samples were allowed to equilibrate at ambient temperature prior to analysis.

To determine pH, 50 ml of sample water was placed in a 100 ml plastic beaker and stirred magnetically. An insulating pad was placed between the beaker and magnetic stirrer to limit heat transfer. Equilibration of pH required 60-90 minutes, and the data were recorded after the pH reading remained stable for a minimum of three minutes.

3.3.2 Conductivity

Conductivity as umhos/cm was determined using a cell-type conductivity meter (Lab Line Lectro-Mho-Meter, Model MC-2 Mark IV). All samples were analyzed for conductivity within three days after field sampling. Samples were either allowed to equilibrate at standard temperature ($25^{\circ}C$) prior to determination or the data were corrected to $25^{\circ}C$ using linear correlations developed in the laboratory.

3.3.3 Alkalinity

Acid neutralizing capacity ($[ANC]_{f=0}$,carbonate)is determined by the equivalents of acid required to titrate the solution to a known equivalence point or proton reference level and is the parameter measured by the Gran

titration. In carbonate dominated systems alkalinity, defined as $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$, is equal to $[ANC]_{f=0}$. Since in the pH range 5.5 to 9.5, $[HCO_3^-]$ is much greater in concentration than the other constituents its molar concentration can be assumed to equal alkalinity. There was no significant difference in analytical results by choosing one parameter over the other.

Alkalinity ($[ANC]_{f=0}$ for the carbonate system) was determined by potentiometrically titrating a 50 ml water sample with 0.02N HCl using an adjustable micropipettor. Samples were stirred at low speed to limit CO_2 stripping during the titration. A minimum of five and up to fifteen titration data points (total equivalents of acid vs. pH) were regressed to determine the $[ANC]_{f=0}$ equivalence point using linear Gran functions. (Gran, 1950; Stumm and Morgan, 1981). All linearly regressed titration data points were within the pH range 3.5 to 5 to limit both weak base and hydrogen activity errors inherent in this method (Driscoll and Bisogni, 1982). Analyses were normally performed in duplicate, but in triplicate if the relative error between duplicates exceeded 10%. Results typically agreed within 5% of the mean. Standard solutions of 40 meq/L $[ANC]_{f=0}$ were titrated to verify acid normality. $[ANC]_{f=0}$ determinations were completed within five days after field sampling.

3.3.4 Major Cation Metals

Analyses for major cation metals (Ca^{2+}, Mg^{2+}, Na^+, K^+) were performed using an atomic absorption spectrophotometer (Perkin-Elmer Model 360). The ten second integrating cycle was used for quantification. Lanthanum (2.5% in 50% HCl) was added to the samples and standards to eliminate interferences associated with the ionization of alkaline earths, dissolved

silica, and aluminum. A double glass distilled water blank was carried through all analyses to provide a basis for background correction. Samples were pretreated by filtration through a 0.1 um membrane filter and therefore reflect dissolved concentrations. Detection limits of 150 ug/L calcium, 15 ug/L sodium, 13.5 ug/L potassium, and 6 ug/L magnesium were obtained by this method.

3.3.5 Fluoride

Fluoride analyses were performed using a fluoride specific ion electrode (Orion Model 96-09) and an Orion Ionanalyzer (Model 801) capable of reading to 0.1 millivolts. To eliminate error induced by changes in fluoride activity, 50 ml of low level total ionic strength adjusting buffer (TISAB) was combined with 50 ml of sample (Orion, 1977B). Fluoride response was linear with concentration down to 100 ug/L and curvilinear from 100 ug/L to the detection limit of 1 ug/L. At the low concentrations encountered in most lake samples, electrode equilibration required between 20 and 45 minutes.

3.3.6 Aluminum

3.3.6.1. Aluminum Analyses

Aluminum was analyzed by an adaptation of Barnes (1975) method (La Zerte, 1984). Aluminum in a 200 ml filtered sample was complexed with 2 ml of 5% 8-hydroxyquinoline and buffered at pH 8.3. The resulting complex was then extracted into 10 ml of methylisobutylketone (MIBK) by mixing for 10 seconds followed by 3 to 5 minutes separation. The lower aqueous layer was then drawn off using a separatory funnel and discarded. The organic layer

was stored at 4°C in dark brown glass vials until analysis. Aluminum determinations were made using a spectrophotometer (Heath Series 700) at 395.01 nm using 1 cm quartz cells.

Reaction time of aluminum extraction was minimized by the ten second mixing time. Therefore, only the monomeric (free or complexed) aluminum species that can be considered as equilibrium species were removed (Barnes, 1975; Smith and Hem, 1972).

Surface samples were fractionated between the operationally defined labile (inorganic) and nonlabile (organically-complexed) aluminum by passing an aliquot through a column of strongly acidic cation exchange resin (Amberlite C.G.-120). The column was regenerated with 10^{-3} M NaCl before each sample separation to maintain the resin in the sodium form. The flow rate was maintained above 25 ml/min to limit the disruption of labile complexes within the resin (Driscoll, 1984). Organic ligands form strong complexes with aluminum and are presumed to be anionically or nonionically charged, thus effectively competing with the exchange resin. The free and inorganically complexed aluminum are readily removed from solution by the polar resin. The pH change associated with the cation exchange treatment is sufficient to disrupt the cationically charged inorganic ligands ($Al(OH)_2^+$) but will only affect the nonlabile monomeric aluminum to a limited extent (Driscoll, 1984). The nonlabile aluminum is measured directly in the column eluate. The difference between total monomeric aluminum and nonlabile aluminum is termed inorganic aluminum. This fraction includes free aluminum as well as hydroxide, fluoride, and sulfate complexes of aluminum.

3.3.6.2 Storage Procedure

Aluminum storage procedures were tested for accuracy and time-induced

error. The standard curve was found to be linear down to 7 ug/L and logarithmic below 7 ug/L to a detection limit of 0.35 ug/L. Eighty-one percent of the samples fell on the nonlinear part of the curve. The standard error of 0.28 ug/L on the lower portion of the curve resulted in a 95% confidence interval of less than 20% of the mean.

Field-fixed samples that were stored three months, then reanalyzed, averaged 11% higher total aluminum concentration than the original determination. This change is not considered important when compared to the original confidence interval for aluminum determination of 20% of the mean. Aluminum fixed three months after sample collection averaged 26% lower than the original sample (fixed three to four hours after collection) and had an increase in the confidence interval to 36% of the mean. Apparently some monomeric aluminum was "lost". Aluminum samples for the July trip were fixed upon returning to the laboratory one to three weeks after sampling and may therefore be slightly underestimated. Recent research indicates the loss of aluminum is associated with the organically complexed fraction (Sullivan et. al., 1986). Equilibrium may also have shifted in favor of the polynuclear aluminum species not determined by this method (Barnes, 1975, Sullivan et. al., 1986).

3.3.7 Chloride

Chloride ion concentration was determined potentiometrically in accordance with Standard Methods No. 407 B (A.P.H.A., 1983).

3.3.8 Sulfate

Sulfate concentration was determined using a variation of the turbidimetric method (A.P.H.A., 1983) as described by Nelson and Delwiche

(1983). A turbidity meter (Hach Model 2100-A) was used for turbidity measurement.

The turbidimetric method involves the addition of barium chloride to the sample, causing the precipitation of the less soluble barium sulfate. The conditioning agent described in Standard Methods, normally used to assure crystals of uniform size, was not used in this procedure because of its associated background turbidity. Eliminating the background turbidity increased the precision, lowered the detection limit, and increased the reproducibility of this method (Nelson and Delwiche, 1983). The standard curve however, is exponential rather than linear due to the larger barium sulfate crystals at higher concentrations. As a result, numerous standards were required to define the curve in the sampling range. The detection limit was <0.05 mg/L as SO_4^{2-}.

3.3.9 Total Dissolved Organic Carbon (DOC)

Samples were filtered through pre-combusted glass fiber filters (Whatman 934-AH). DOC was determined instrumentally by CO_2 infrared absorbance of wet oxidized dissolved organic carbon (Oceanography International Model 0524AA Carbon Analyzer) and prepared in accordance with the Oceanography International Carbon Analyzer Instrument Manual. All ampules used for samples or standards were precombusted at 500°C for 12 hours. Samples were analyzed for DOC with storage time ranging from three to five months. The detection limit was 0.5 mg/L as carbon with a standard error equal to 17% of the mean.

3.3.10 Silica

Dissolved silica concentrations were determined spectrophotometrically (Bausch and Lomb Spectronic 88) at 815 nm using the heteropoly-blue method

(Standard Methods No. 425 D, A.P.H.A., 1983). The detection limit was 0.02 mg/L as SiO_2.

4.0 RESULTS

The lakes sampled in this study may be characterized as weakly buffered, with an extremely dilute ionic composition (conductivity range 3.6 to 56.3 uhmos/cm). Calcium was the dominant cation, constituting 76.4% of the total cations on a equivalent basis, followed by sodium, 16.26%; magnesium, 6.02%; and potassium, 1.32%. Bicarbonate dominated the anions, accounting for 80.04% on an equivalent basis followed by sulfate, 10.12%; and chloride, 6.47%. Composited lake surface water chemistry data are summarized in Table 4, with individual lake water chemistry data summarized in Appendix 3.

4.1 Limnology

Limnological data is presented in Appendix 1. Lakes appeared to reach a thermal maximum in July or August and decrease in temperature by September. Stratification is more pronounced in July than September. Fall turnover appears to have been completed by September, with only Golden Lake remaining stratified at the end of the summer. Dissolved oxygen concentrations generally increased as lake temperatures decreased.

Temporally sampled lakes had lowest alkalinities in July, increased to a maximum in August and generally showed a decrease by late September as shown in Figure 2. The most significant variation in alkalinity occurred in small volume to watershed area lakes. The higher volume to watershed area ratios of Golden and Mowich lakes result in longer hydraulic residence times which dampen seasonal events (Welch et al., 1985).

Figure 2

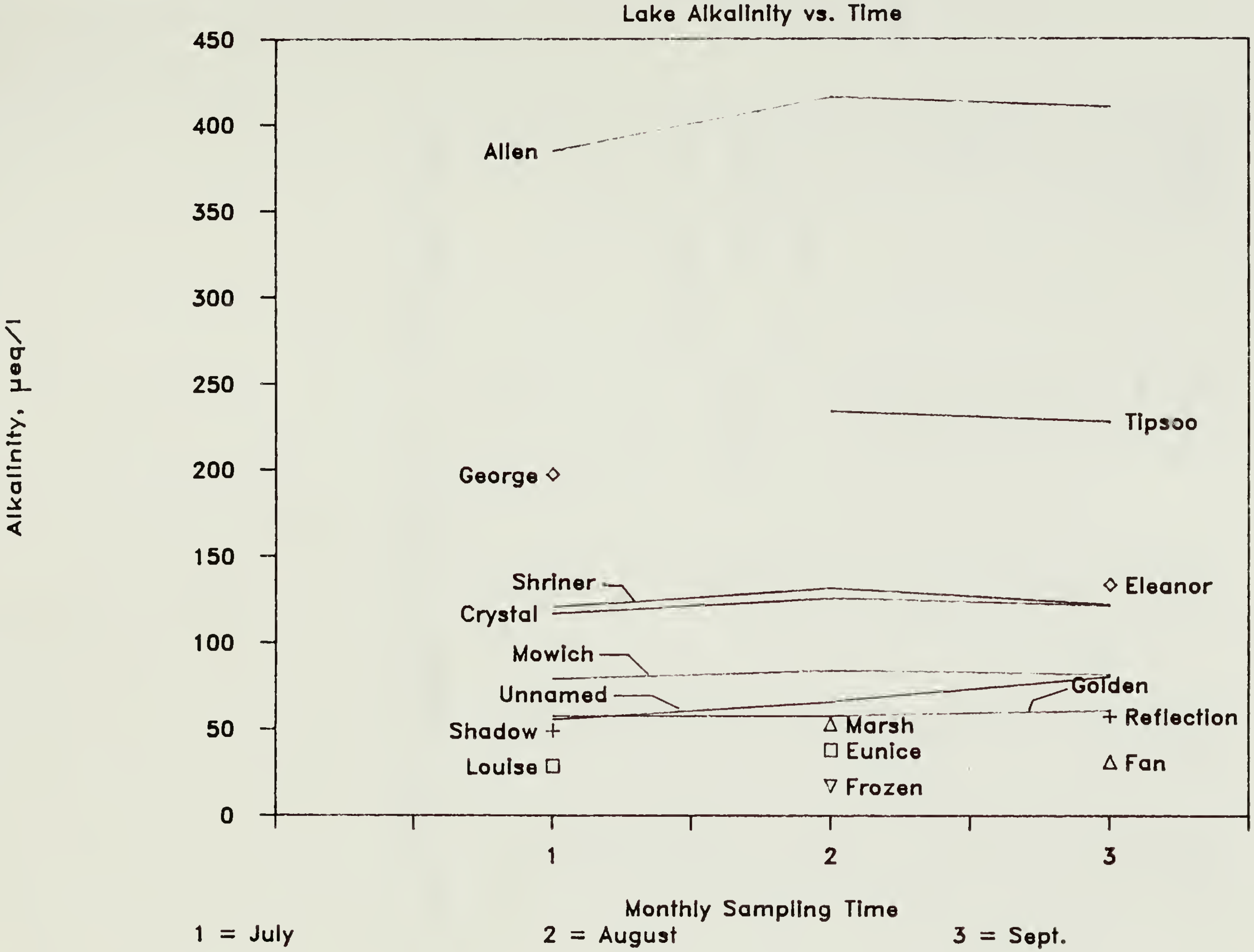

Lake Alkalinity vs. Time
Alkalinity, μeq/l
450
400
350
300
250
200
150
100
50
0
1
2
3
Monthly Sampling Time
1 = July
2 = August
3 = Sept.
Allen
Tipsoo
George ◇
◇ Eleanor
Shriner
Crystal
Mowich
Unnamed
Golden
Shadow +
+ Reflection
△ Marsh
□ Eunice
▽ Frozen
Louise □
△ Fan

Table 4

Composited Water Chemistry Summary for Lake Surface Samples*

Parameter	Units	Max.	Min.	Avg.
Alkalinity	ueq/L	404	17	106
$[SO_4^{2-}]$	ueq/L	99	0	14
$[Ca^{2+}]$	ueq/L	403	10	93
$[Mg^{2+}]$	ueq/L	27	0.7	6.4
$[Na^+]$	ueq/L	32	10	19
$[K^+]$	ueq/L	3	0.5	1.4
Anion/cation ratio		1.26	0.88	0.99
Conductivity	umho/cm	56.3	3.6	16.2
$[HCO_3^-]/[cations]$		1.0	0.76	0.86
pH (field)		7.3	5.3	6.35
pH (lab)		7.5	5.6	6.6
DOC	mg/L	3.09	0.5	1.3

* Lakes sampled multiple times were averaged prior to computing the overall summary. All values are sea salt corrected.

The drop in alkalinity seen in September for most temporally sampled lakes is often associated with fall turnover (Lazerte, 1984).

There was a definite increase in alkalinity and a generally greater ion concentration with depth in all lakes. The deeper samples (generally below the thermocline) exhibited better correlation coefficients between ion concentrations and conductivity than did their surface sample counterparts, indicating a greater dependence of ionic composition on mineral dissolution. These profiles are generally consistent with the physical behavior of dimictic lakes and suggest that during the summer, water more typical of groundwater, without precipitation dilution, accumulates in the hypolimnion (Welch et al., 1985).

4.2 pH

The range of pH values determined for lakes in this study was 5.2 - 7.4 in the field and 5.6 - 7.6 for lab equilibrated samples. Lab-equilibrated pH averaged 0.08 pH units higher than field pH with a standard deviation of 0.012 pH units. Empirically derived equations correlating the parameters measured in this study to lab-equilibrated pH are listed in equations 1-16 (App. 2). Parameters are sea salt corrected and expressed in ueq/L except where noted.

4.3 Conductivity

The average conductivity, for all samples, of 22.7 umhos/cm reflects this dilute nature of the lakes studied. Conductivity ranged between 3.4 and 83.0 umhos/cm with a standard deviation of 19.8 umhos/cm. Conductivity is strongly correlated with ionic strength ($r^2 = 0.98$) and therefore provides an indirect measurement of the water's overall ionic composition.

A strong correlation between conductivity and individual ionic concentrations indicates weathering reaction genesis. Only total aluminum and chloride showed no significant correlation with conductivity ($r^2 \leq 0.30$). Correlation coefficients for all of the ion concentration to conductivity equations increased with lake depth.

The correlation between ionic strength (mole/L) and conductivity (umhos/cm) for this study ($I = -3.09 + 1.44 \times 10^{-5}$ x cond; eq. 28) is similar to both the equation determined for the Oregon Cascade lakes ($I = 1.28 \times 10^{-5}$ x cond; Nelson and Delwiche, 1983) and the equation cited by Snoeyink and Jenkins (1980) for surface waters in general ($I = 1.6 \times 10^{-5}$ x cond.). Activity coefficients of 0.98 and 0.935 for monovalent and divalent ions, respectively, were calculated by the Debye-Huckel limiting law for the mean lake ionic strength. Errors incurred by using concentrations rather than activities are small and generally within the analytical uncertainty of the data.

4.4 Alkalinity

The mean alkalinity for all samples was 162 ueq/L with a range of 10.0 to 693.5 ueq/L and a standard deviation of 165 ueq/L. For lake surface samples the median and average alkalinities ($[HCO_3^-]$) were 62.5 ueq/L and 106, ueq/L respectively. These results are similar to those found by Welch and Chamberlain (1981) for 18 lakes north of Mount Rainier in Western Washington state (median = 73 ueq/L and average 113 ueq/L).

Alkalinity correlations with measured parameters are listed in equations 29-41 (App. 2). Alkalinity as a function of lab pH and of field pH are illustrated in Figures 3 and 4, respectively. Lake data is plotted and identified by sample depth. The theoretical alkalinity vs. pH equation

Figure 5. Alkalinity vs. Lab pH

All Samples

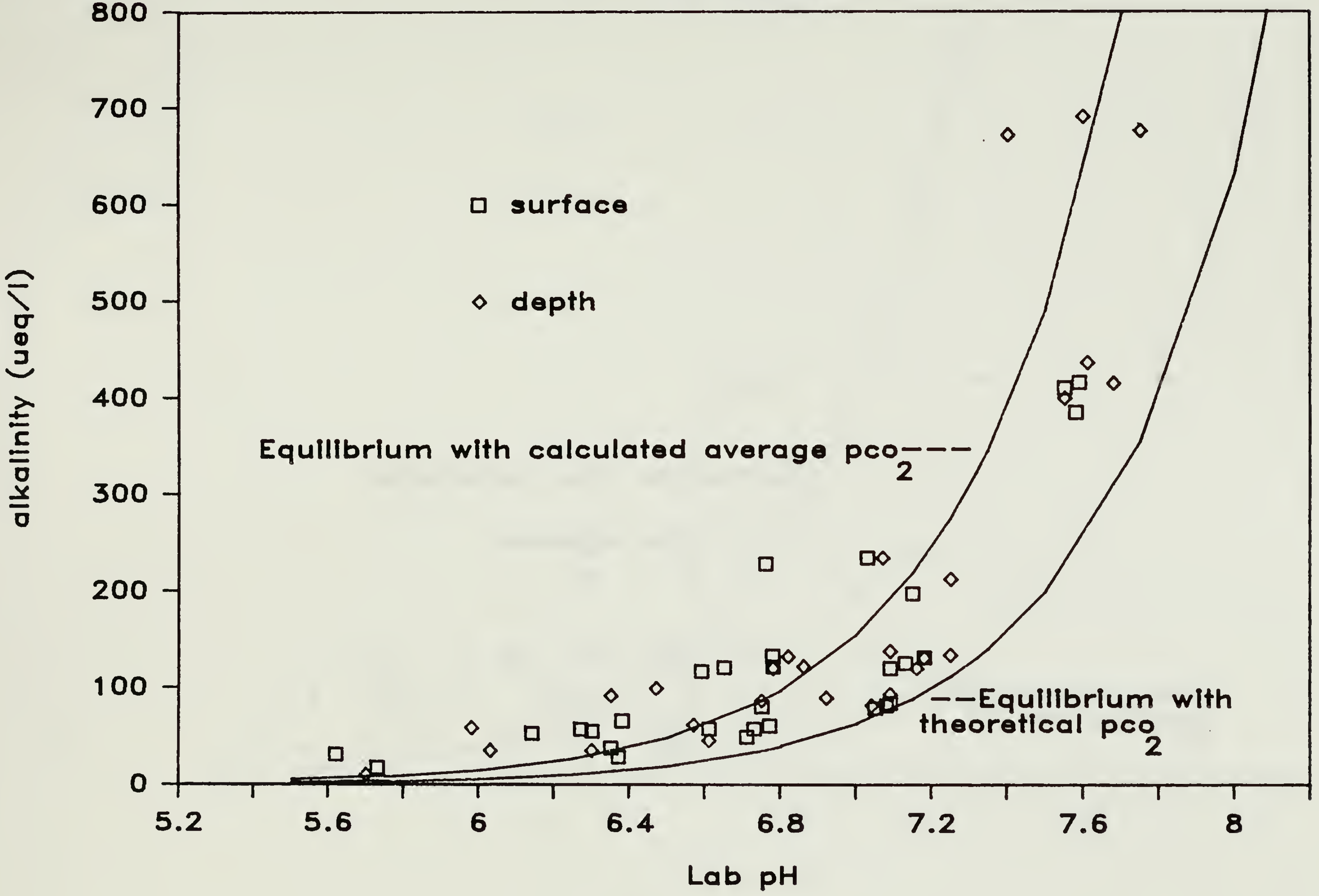
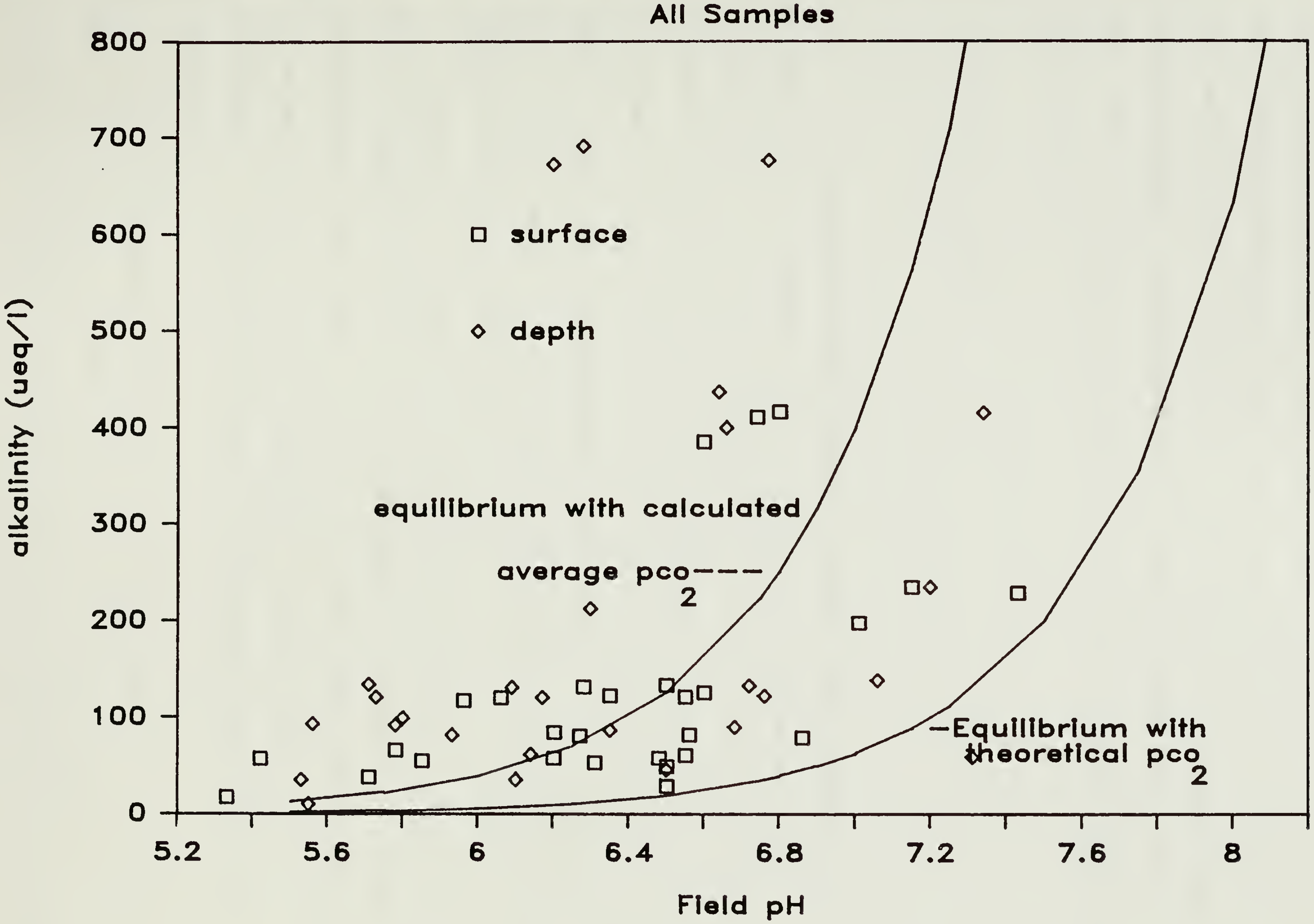


Figure 4. Alkalinity vs. Field pH



for mean sea level $p_{CO_2} = 10^{-3.5}$ atm. is included for comparison. The data more closely correlate with the theoretical equation (eq. 16, Table 1) when lab-equilibrated pH is used. Points falling above the theoretical line indicate either equilibration at a higher CO_2 partial pressure, such as from groundwater, or the presence of an additional weak buffering system. These relationships are discussed in the section entitled "Buffering System" (Sec. 5.3).

4.5 Major Cation Metals

4.5.1 Calcium

Calcium concentrations averaged 2.8 mg/L, ranged between 0.2 and 8.6 mg/L and had a standard deviation of 2.9 mg/L. Calcium was the dominant cation in all but a few exceptionally dilute lakes where sodium dominated. Strong correlations were found between calcium and alkalinity, conductivity, and lab equilibrated pH ($r^2 \geq 0.81$). Calcium increased with depth for almost all lakes and surface concentrations increased over the summer sampling period. Of the cations, calcium most closely reflected the temporal variations of alkalinity.

A comparison of alkalinity to calcium ratios for several geographical areas is presented in Table 5. This relationship is remarkably consistent for Washington Cascade lakes. Logan et al. (1983) concluded that, assuming similar geology, the similarity in equations indicates either no acidification or consistent magnitudes of acidification among Washingtion Cascade Lakes.

Similar to the more rigorous electroneutrality equation, the intercept term of these simplified equations may be used with caution to indicate strong acid concentrations. The greater the effect of strong acid, the more

negative the intercept term. Apparently there is a minimal effect of strong acid deposition on Washington and Oregon lakes. The significantly lower intercept term for the described regression applied to Adirondack lakes (New York) data indicates the greater effect of acids and probable anthropogenic influences on their water chemistry (cited in Nelson and Delwiche, 1983).

Table 5

Alkalinity vs. Calcium for Several Geographical Areas

Region	Equation $(y=I_o+b(x))$	Correlation Coeff., r^2	Source
Mt. Rainier	$[Alk] = 1.83 + 1.09[Ca^{2+}]$	0.97	This Study
Central Washington Cascades	$[Alk]=-5.77+1.07[Ca^{2+}]$	0.96	Logan et al., 1982
North Washington Cascades	$[Alk]=2.67+0.995[Ca^{2+}]$	0.98	Logan et al., 1982
Oregon Cascades	$[Alk]=-3.70+2.40[Ca^{2+}]$	0.88	Nelson and Delwiche, 1983
California Cascades	$[Alk]=12.775+0.8518[Ca^{2+}]$	0.97	Melack et al., 1985
Experimental Lakes Western Ontario	$[Alk]=-32.0+1.42[Ca^{2+}]$	0.76	Henricksen, 1979
Northern Norway	$[Alk]=-29.0+1.32[Ca^{2+}]$	0.85	Henricksen, 1979
Adirondack lakes	$[Alk]=-94.9+0.94[Ca^{2+}]$	N/A	Driscoll, 1980

Data not sea salt corrected.
N/A = not available.

4.5.2 Magnesium

Magnesium concentrations for all samples averaged 0.31 mg/L, ranged between 0.02 and 1.17 mg/L, and had a standard deviation of 0.30 mg/L. Magnesium was found to be closely correlated with alkalinity (r^2 = 0.92), and conductivity, (r^2 = 0.93) and have a fair correlation with pH (r^2 = 0.73). Correlation coefficients were less than those for calcium but greater than those for sodium and potassium.

4.5.3 Sodium

Sodium concentrations for all samples averaged 0.70 mg/L, had a range of 0.24 to 2.24 mg/L and a standard deviation of 0.39 mg/L. Sodium showed a weak correlation with pH (r^2 = 0.31) and fair correlations with both conductivity (r^2 = 0.67) and alkalinity (r^2 = 0.73). Stepwise multiple regression showed a significant correlation increase when sodium was included as a component relative to alkalinity. Therefore a significant amount of sodium appears to be derived from mineral dissolution with bicarbonate as a counterion.

4.5.4 Potassium

Potassium concentration for all samples averaged 0.10 mg/L, had a range between 0.02 to 0.71 mg/L and a standard deviation of 0.14 mg/L. Potassium showed only weak correlations with conductivity (r^2 = 0.43) and alkalinity (r^2 = 0.53) and a low correlation with pH (r^2 = 0.22). Similar results were reported for the Oregon Cascades (Nelson and Delwiche, 1983). Despite its relatively low concentration (1.3% of cations) stepwise multiple regression shows potassium to be the most significant counterion for alkalinity, after calcium. This indicates that potassium is the product of weathering

reactions.

The poor correlation coefficients for potassium may also reflect error induced by incorrect sea salt estimates. Potassium in aerosols is greatly influenced by terrestrial dusts which are not accounted for by sea spray corrections, as applied. Due to the low potassium concentrations, this error may be significant.

4.5.5 Total Cations

Total cations (not sea salt corrected, surface and depth samples) averaged 200.4 ueq/L, ranged between 21.8 and 741.8 ueq/L and had a standard deviation of 185 ueq/L. On a sea salt corrected equivalent basis the Ca:Na:Mg:K ratio is 80.0:13.2:5.5:1.3. Multiple regression showed that all major cations are positively correlated with bicarbonate and increase the correlation coefficient in the descending order of significance. Ca>K Na Mg. This indicates that the dominant cations are all counterions for bicarbonate in weathering reactions (Zimmerman, 1982).

High correlations were found between total cations and alkalinity (r^2 = 0.99), conductivity (r^2 = 0.99), and pH (r^2 = 0.77).

In acidified Adirondack lakes hydrogen and aluminum account for average of 23% of the total cation concentration (Driscoll, 1980). The relative cation contribution of hydrogen and aluminum ions was negligible in this study.

4.6 Sulfate

Sulfate averaged 1.09 mg/L, with a range of 0.1 to 6.2 mg/L and a standard deviation of 1.5 mg/L. Sulfate had a weak positive correlation with conductivity (r^2 = 0.46), and low correlations with pH and alkalinity.

These relationships are greatly affected by apparent indigenous sulfate sources at Allen Lake. When Allen Lake data is disregarded, sulfate correlation with conductivity is poor ($r^2 \leq 0.15$).

Sulfate concentrations did not increase with lake depth. The lack of conductivity, alkalinity, or spatial correlations for sulfate indicates that weathering reactions are not a significant source of sulfate. Local sources of sulfate resulted in a negative correlation between pH and $[SO_4^{2-}]$ in the Alpine Lakes Wilderness Area of Washington. Similarly, when local sources were disregarded, no correlation of sulfate with pH was evident (Welch and Chamberlain, 1981). No significant correlation was found between $[SO_4^{2-}]$ and other parameters in Oregon Cascade lakes (Nelson and Delwiche, 1983).

4.7 Chloride

Chloride averaged 0.42 mg/L with a range of 0.0[illegible] to 1.12 mg/L and standard deviation of 0.22 mg/L. Chloride accounted for an average of 6.[illegible]% of the total anions on an equivalent basis and showed little variation in concentration. No significant correlation existed between chloride and pH, conductivity, or alkalinity ($r^2 \leq 0.22$). Sea spray appears to be the dominant source of chloride in the study lakes. Sea salts (based on $[Cl^-]$) accounted for 11.5% of total cations and 11.1% of the anions (equivalent basis) in the study lakes.

4.8 Fluoride

Fluoride concentration averaged 15.2 ug/L with a range of 6.5 to 40 ug/L and a standard deviation of 5.5 ug/L. Fluoride concentration was positively correlated with conductivity and alkalinity, but not pH. Driscoll (1984) suggested that aluminum complexation controls fluoride

concentrations in Adirondack lakes. At the low pH of Frozen Lake, nearly 30% of the fluoride present was estimated to be complexed with aluminum. However, at the pH ranges generally encountered in this study, aluminum fluoride complexes averaged less than 0.02% of total fluoride. Average fluoride concentrations of 15 ug/L are similar to the 11.8 ug/L found in Oregon Cascade lakes (Nelson and Delwiche, 1983) and are probably background levels.

4.9 Aluminum

Aluminum concentration for all samples averaged 11.8 ug/L, ranged between 0.7 ug/L and 90 ug/L with a standard deviation of 25 ug/L. For surface samples that were fractionated, total aluminum averaged 13.2 ug/L, nonlabile (organically complexed) aluminum averaged 2.7 ug/L, and labile aluminum averaged 10.6 ug/L. Total aluminum was only weakly correlated with alkalinity, conductivity, or pH ($r^2 \leq 0.35$). Similar or improved correlations with aluminum were found for silica, DOC, and field pH. Multiple regression indicated that over 65% of the variation in aluminum concentration could be accounted for by variation in DOC and field pH. This relationship remained consistent for surface and depth samples and was not improved by the addition of any other parameters.

Surface aluminum samples were fractionated into organic and labile aluminum components. The organically complexed aluminum showed a good correlation with DOC ($r^2 = 0.79$) and was independent ($r^2 \leq 0.25$) of any other parameter. The labile (inorganic) aluminum component showed a weak correlation with DOC ($r^2 = 0.44$) and a still weaker correlation with pH ($r^2 = 0.37$).

4.9.1 Aluminum Speciation

The water chemistry data for aluminum were examined with respect to theoretical thermodynamic and mass balance relationships as previously summarized (Table 2) using the MICROQL computer program developed by Westall (1979). In general, fluoride and sulfate complexes with aluminum were negligible. Fluoride complexes often become the dominant form of aluminum below pH 5.5 (Driscoll et al., 1984). Only Frozen Lake and Golden Lake's July sample were predicted to have significant aluminum fluoride complexation. The predominant aluminum ligand was hydroxide under the conditions encountered in this study.

Free aluminum concentrations ($[Al^{3+}]$) calculated for the observed data when compared to theoretical solubilities for aluminum solid phases appear to be controlled by an aluminum trihydroxide phase similar to natural gibbsite (log K_{so} = -8.88) and less soluble than microcrystalline gibbsite (log K_{so} = -9.35). Calculated free ionic aluminum is plotted versus pH and showing theoretical solubility controls in Figure 5. The solubility constant determined by regression for the lakes in this study (log K_{so} = -8.86) is similar to the constants, log K_{so} = -9.1 and -8.49, empirically determined for lake systems by Cosby et al.. (1985) and Driscoll and Bisogni (1982), respectively.

Figure 6 superimposes the labile (total inorganic) aluminum concentrations on an aluminum solubility diagram in equilibrium with microcrystalline gibbsite. Only one point (Golden Lake, July) would theoretically indicate elevated levels of aluminum ion $[Al^{3+}]$ due to pH values below 5.5. Elevated levels of labile aluminum above pH 6 (Shriner and Tipsoo Lakes) are attributable to $Al(OH)_4$ complex formation as pH increases.

Figure 3. Free Aluminum vs. pH

With Gibbsite Solubility

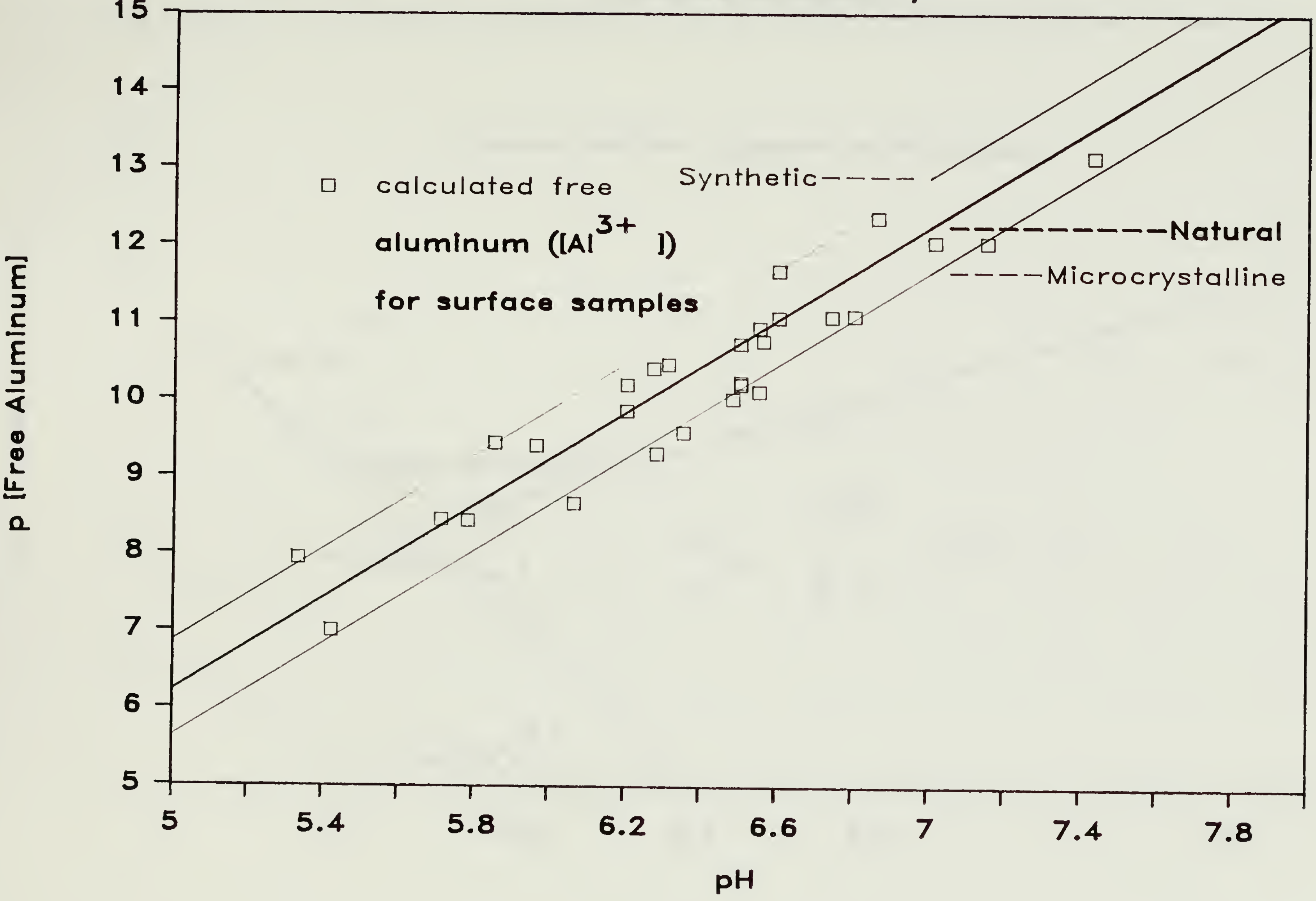
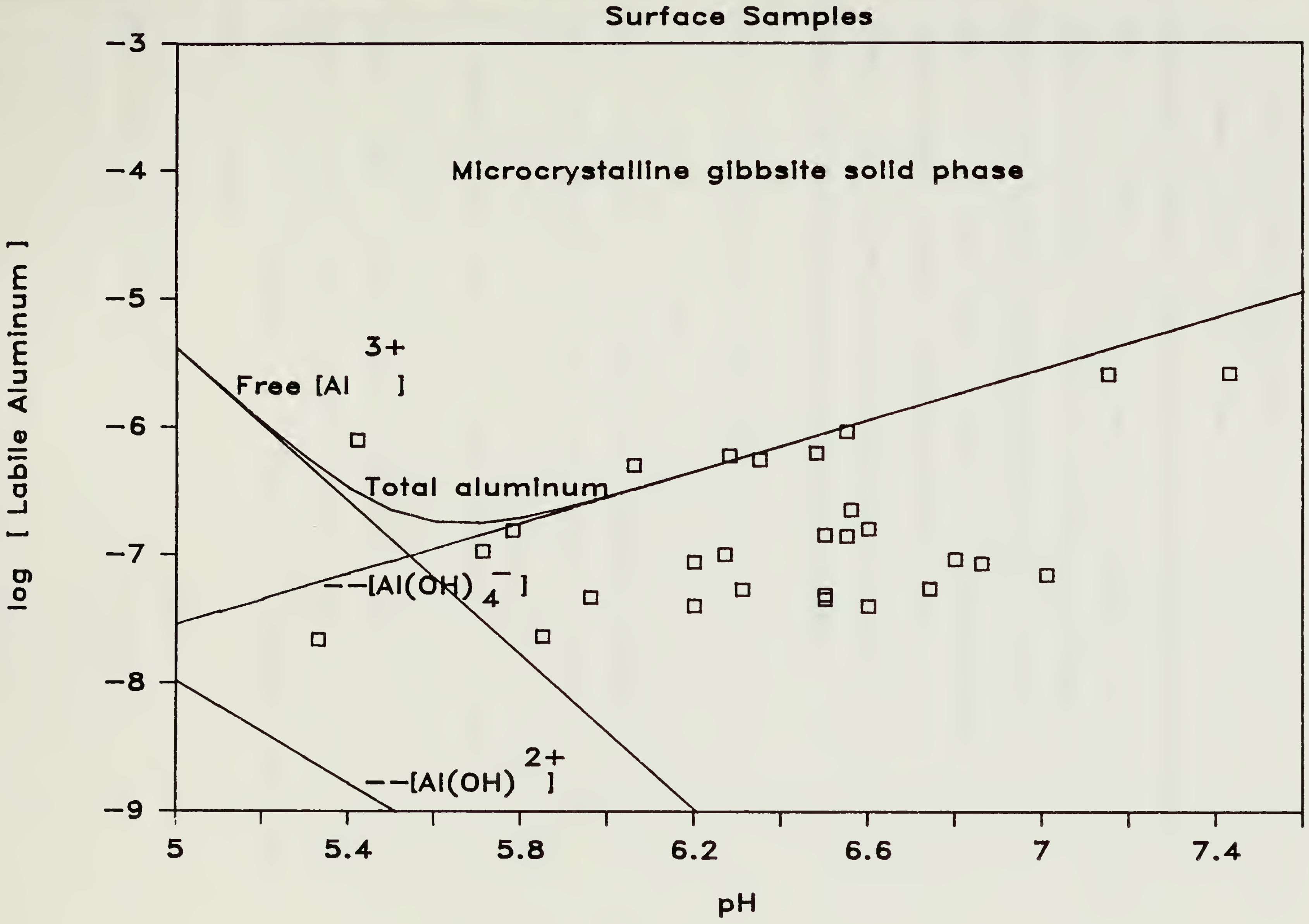


Figure 6. Labile Aluminum vs. pH



4.9.2 Temporal Variation of Aluminum

Aluminum concentrations were lowest in August. The increases in both early summer and fall appear to be largely caused by increases of organically complexed aluminum resulting from increased levels of DOC (Figure 7). When determined seasonally, the apparent solubility constant decreases from log K_{so} = -8.80 to -9.04 from early summer to fall. Although the difference between these two values is probably not significant, it does indicate a trend of decreasing aluminum solubility over the summer. Driscoll (1985) attributed similar results to spring snowmelt events releasing a peak flow of water unlikely to be in equilibrium with any controlling aluminum solid phase.

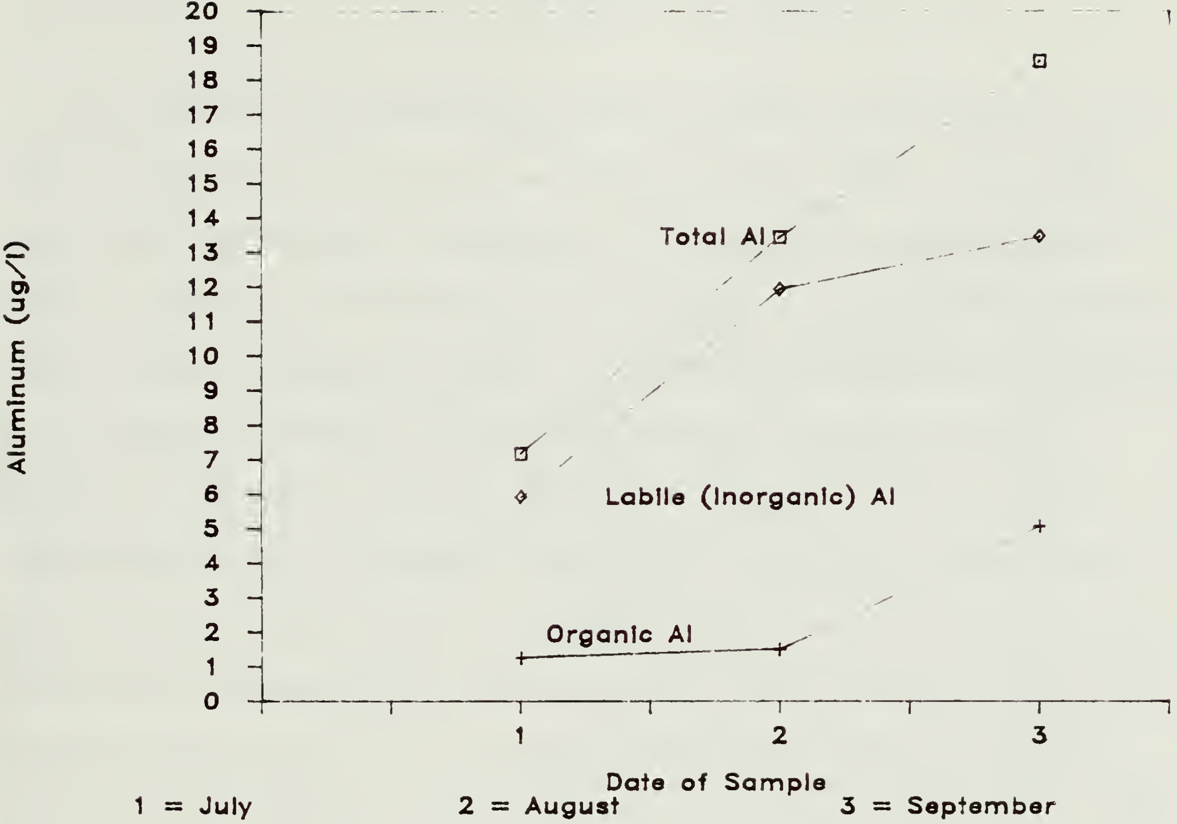
10 Total Dissolved Organic Carbon (DOC)

The average total DOC for all samples was 2.2 mg/L as carbon with a range of 0.005 mg/L to 24.8 mg/L and a standard deviation of 4.9 mg/L. The average lake surface total DOC concentration of 1.31 mg/L as carbon indicates the unproductive nature of the study lakes. A similar range (0.1-3.6 mg/L DOC) was found for six Oregon Cascade lakes; however, four of these lakes had concentrations below the detection limit of 0.1 mg/L (Nelson and Delwiche, 1983). The DOC concentrations were similar to or below levels reported for other dilute systems (Elzerman, 1983). For surface waters, levels of DOC are independent of field pH or any parameter other than organic aluminum.

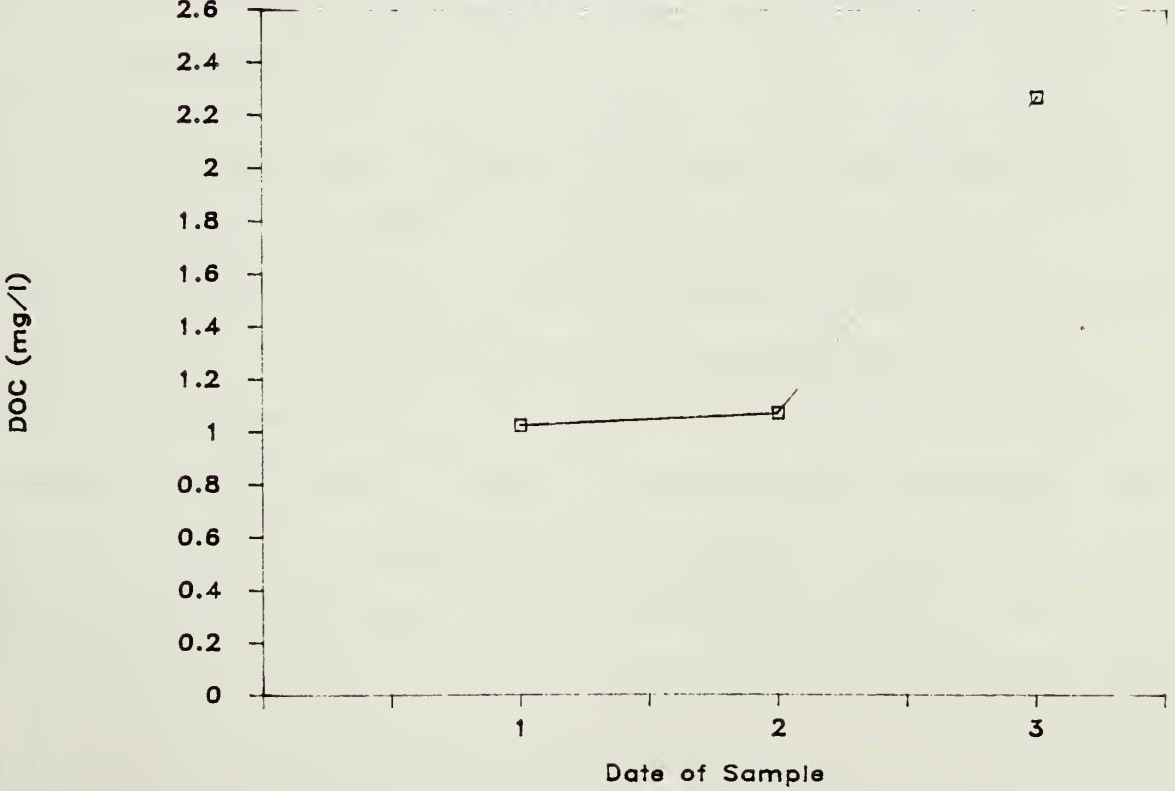
Levels of DOC were an order of magnitude higher in the Golden Lake depth sample than those encountered in the other samples depicted in Figure 7, indicating either high lake productivity or perhaps local production in the soil and runoff into the lake.

Figure 7

a. Average Al Conc. vs. Sampling Date



b. Average DOC Conc. vs. Sampling Date



4.11 Silica

The average silica concentration for all samples was 4.5 mg/L as SiO_2 with a range between 0.8 to 19.1 mg/L and a standard deviation of 3.6 mg/L. Silica exhibited moderate correlations with conductivity and aluminum ($r^2 \geq$ 0.60) and a weak correlation with pH (r^2 = 0.25). Silica either remained stable or showed a general decrease in concentration through July to September, a pattern attributed in other lake systems to uptake by diatoms (Driscoll, 1980; Wetzel, 1975). The low silica concentrations and low correlations between silica and conductivity or alkalinity obtained from surface samples indicate either unreactive bedrock or that much of the lake water enters predominantly as precipitation. Such conclusions should be made with caution due to the biological mediation of the silica cycle (Driscoll, 1980). Silica correlations with conductivity (r^2 = 0.60) and alkalinity (r^2 = 0.67) improved with lake depth, indicating silica's derivation from mineral dissolution.

4.12 Buffer System

Buffer capacity may be defined as the number of equivalents/liter of strong acid which when added to a solution causes a unit change in pH. Figure 8 presents titration curves for five lakes with varying alkalinities sampled in this study. An experimentally determined buffer intensity diagram corresponds directly to the slope of these titration curves and was determined from discrete increments of acid added versus the change in pH as shown in Figure 9. Superimposed on both plots is a hypothetical solution buffered only by the aqueous carbonate system with an alkalinity of 106 ueq/L and an initial pH of 6.8, representing an average lake for this study.

Figure [illegible]: Titration Curves

5 Select Lakes of Differing Alkalinity

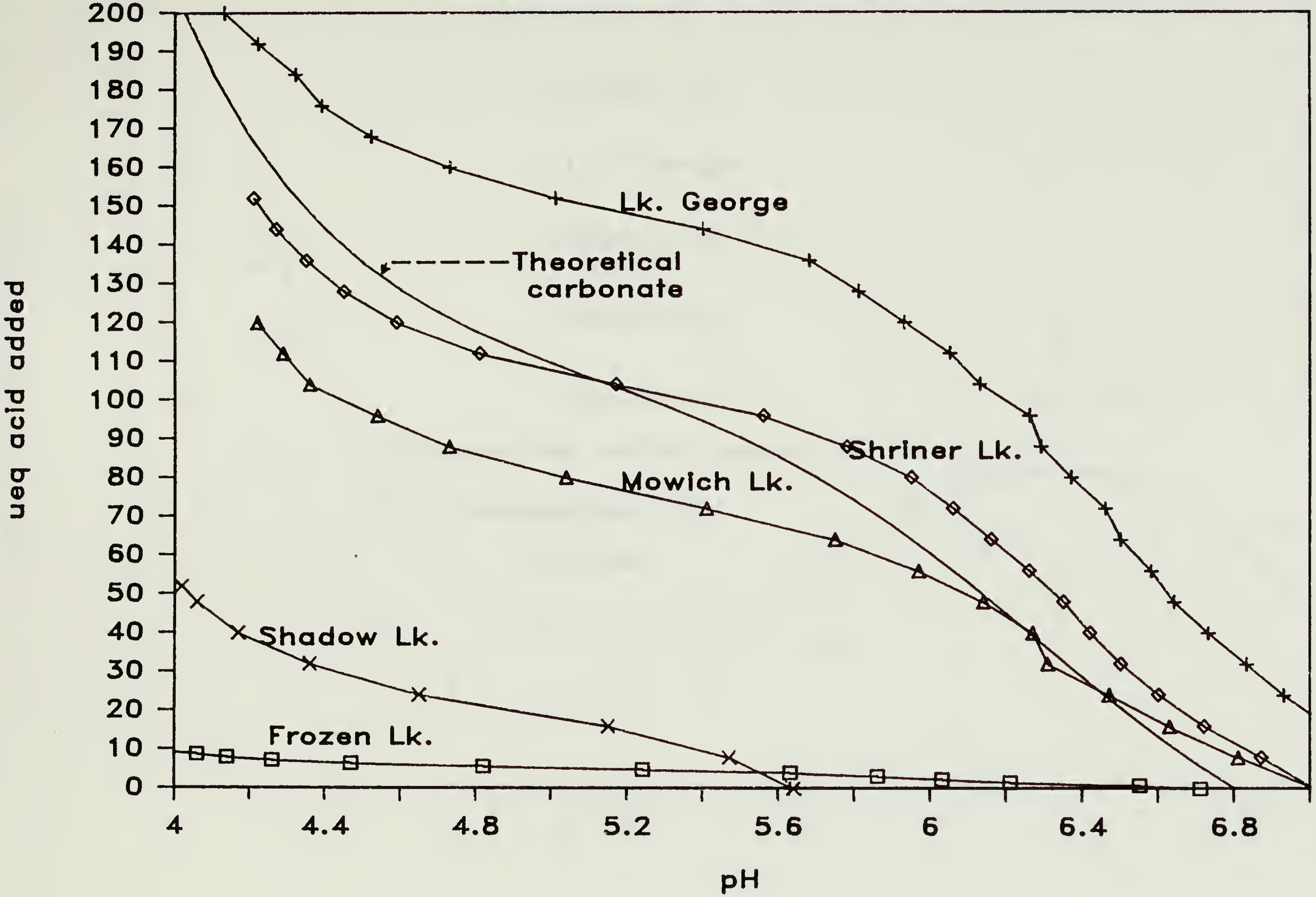
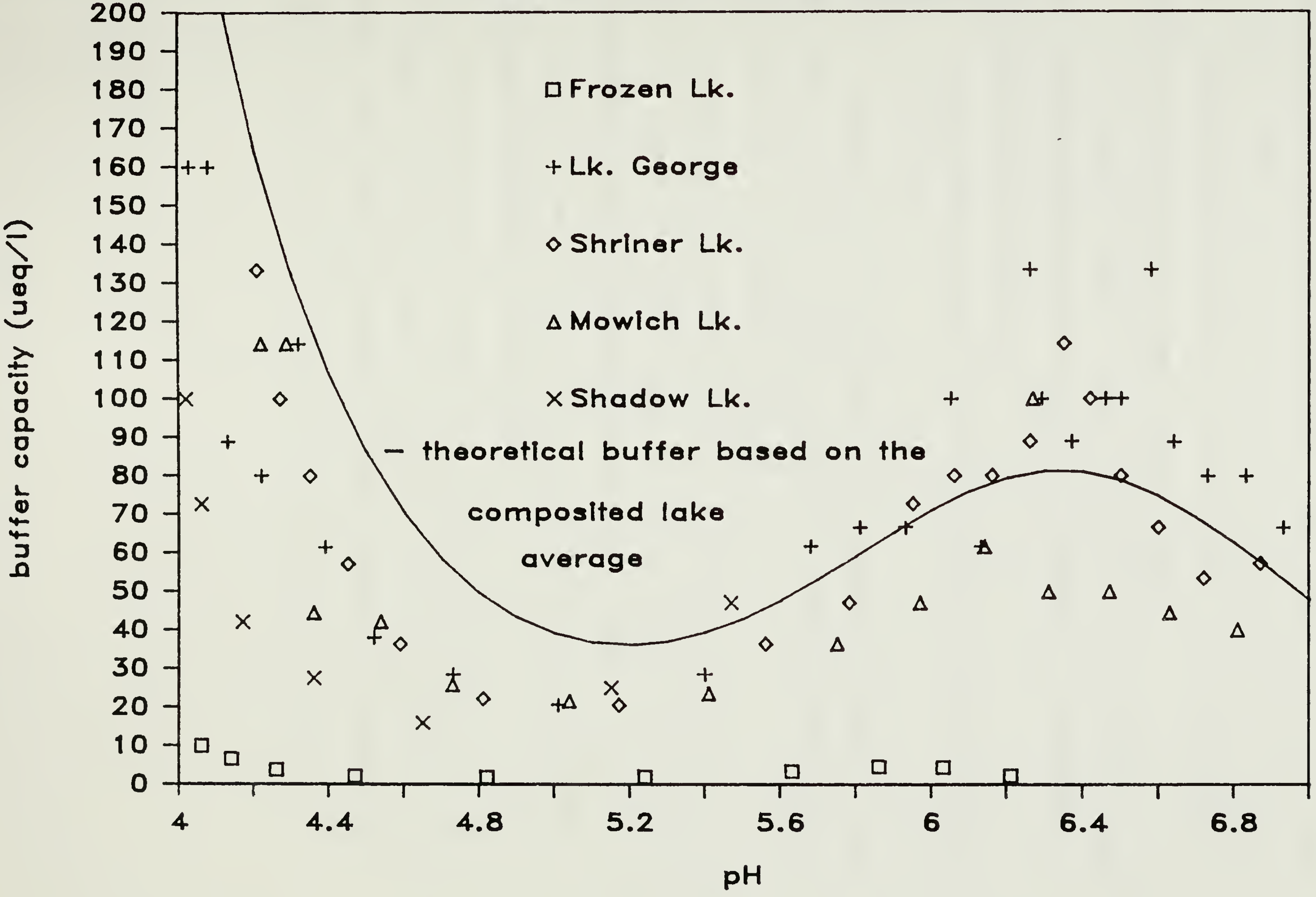


Figure 9. Buffer Capacity vs. pH

5 Select Lakes of differing Alkalinity



The carbonate system, aluminum hydrolysis species, and weak organic acids have been reported as significant buffer systems for dilute lakes (Driscoll, 1980). The carbonate system is dominant above pH values near 5.5. Aluminum hydrolysis species and weak organic acids often become dominant buffers below this point (Driscoll, 1980).

The theoretical buffer intensities of each of these acid-base systems are independently presented in Figure 10. To develop this figure the following assumptions were made:

1) The carbonate system is in open equilibrium with the atmosphere at $P_{CO_2} = 10^{-3.5}$ atm,

2) The water is in equilibrium with an aluminum trihydroxide solid phase with a solubility constant $K_{SO} = 10^{-8.86}$ empirically determined for the study lakes (see Aluminum, Section 4.9.1)

3) DOC (average concentration level 1.0 mg/L) is modeled as an organic acid with an acidity constant, $Ka_{org} = 10^{-4.4}$. A similar model organic acid has been empirically verified by Driscoll et al. (1984)

4) Ionic strength activity corrections, and fluoride and sulfate complexes with aluminum, are negligible.

From Figure 10, in the range of pH values encountered in this study, the dominant buffering systems are carbonate and water. Aluminum hydrolysis species could provide significant buffering intensity at low pH values. Typical DOC levels will probably not provide significant buffering.

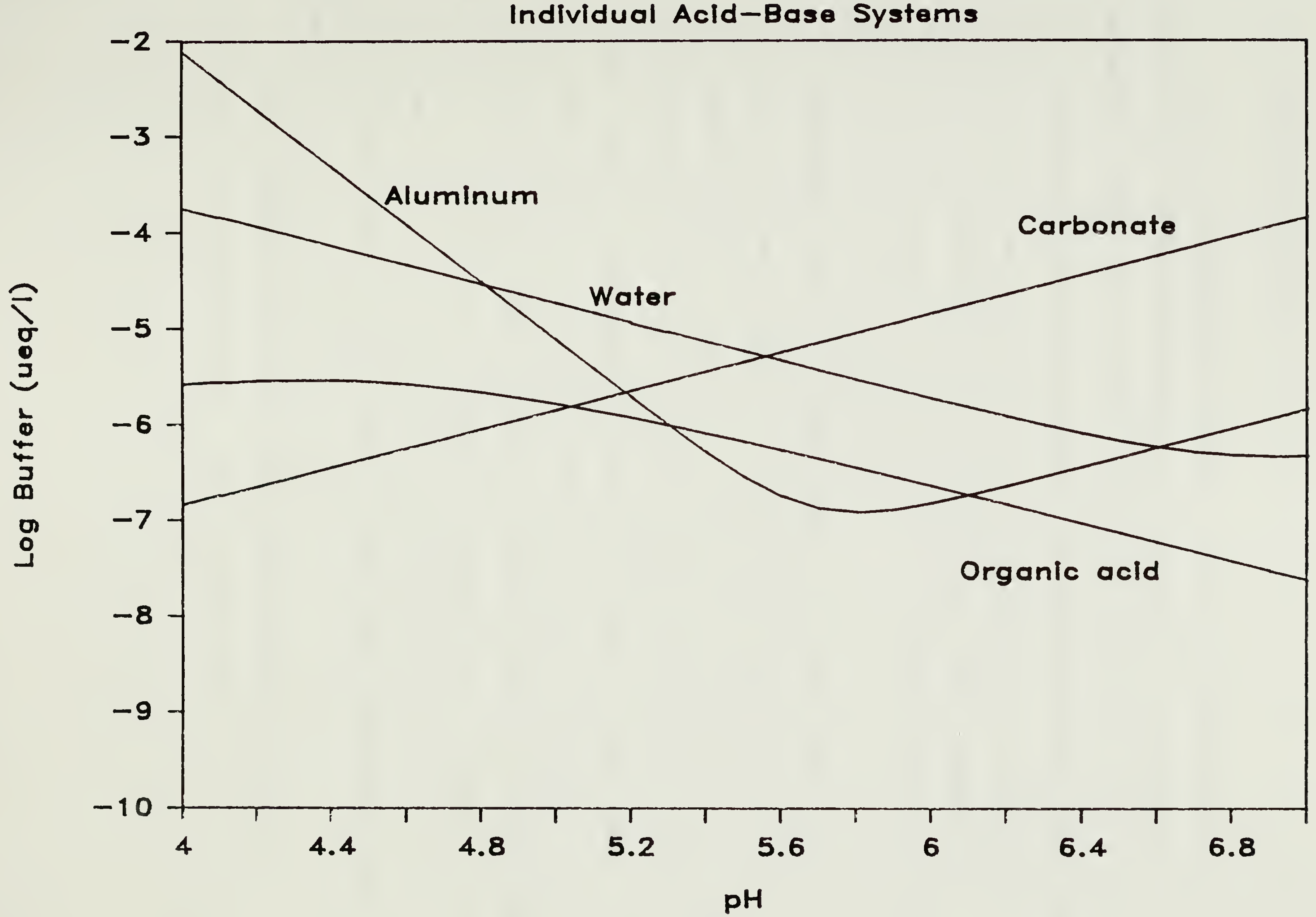


Fig 10. Buffer Capacity vs. pH

5.0 DISCUSSION

5.1 Sensitivity Criteria

Several investigators have proposed criteria for determining lake sensitivity to acidification based on pH, alkalinity, and conductivity parameters. Hendry et al. (1980) proposed that lakes having alkalinities less than 200 ueq/L are highly sensitive, greater than 500 ueq/L alkalinity are nonsensitive, and between 200 to 500 ueq/L alkalinity are moderately sensitive. The Ontario Ministry of the Environment (1981) proposed that lakes having less than 40 ueq/L alkalinity are extremely sensitive and less than 200 ueq/L are moderately sensitive.

Using these criteria for surface samples, four lakes (25%) may be classified as extremely sensitive, ten lakes (63%) highly sensitive, one (6%) moderately sensitive and one lake (Allen Lake, 6%) nonsensitive. Depth samples distributed similarly to surface samples with two lakes (13%) extremely sensitive, nine lakes (60%) highly sensitive, two (13%) lakes moderately sensitive and two lakes (Golden and Allen, 13%) nonsensitive. Zimmerman and Harvey (1979) proposed that sensitive lakes are characterized by pH $\leq$ 6.3, conductivity $\leq$ 40 umhos/cm, and alkalinity $\leq$ 300 ueq/L. Seven lakes had surface and two lakes had both surface and depth samples within these criteria. Only one lake (Allen) and two of three Golden Lake bottom samples exceeded all three criteria.

By all proposed classifications the study lakes are preponderantly highly sensitive to acidic inputs. Only one lake (Allen) is classified as not sensitive. Table 6 below summarizes lake surface sample data compared to these sensitivity criteria.

Table 6

Comparison of Surface Sample Data to Proposed Sensitivity Criteria

Proposed Criteria*

Lake	Ref. 1	Ref. 2	Ref. 3		
			pH	Cond	[Alk]
Golden	high	moderate	+	-	-
Mowich	high	moderate	+	-	-
Unnamed	high	moderate	-	-	-
Shriner	high	moderate	-	-	-
Crystal	high	moderate	-	-	-
Allen	moderate	nonsensitive	-	+	+
Louise	high	extreme	-	-	-
Shadow	high	moderate	-	-	
George	high	moderate	-	-	-
Marsh	high	moderate	-	-	-
Tipsoo	moderate	moderate	+	-	-
Frozen	high	extreme	-	-	-
Eunice	high	extreme	-	-	-
Reflection	high	moderate	-	-	-
Eleanor	high	moderate	-	-	-
Fan	high	extreme	-	-	-

* Refer to text for explanation of criteria.

high = highly sensitive
moderate = moderately sensitive
extreme = extremely sensitive
+ = exceed (nonsensitive)
- = below (sensitive)

References:
1. Hendry et al., 1980
2. Ontario Ministry of the Environment, 1981
3. Zimmerman and Harvey, 1979

5.2 Temporal and Spatial Trends

Both biogenically produced alkalinity and replacement of dilute snowmelt with ground water have been postulated as the reasons for increased alkalinity over the summer months. Of the six lakes temporally studied, five showed an increase in DOC, indicating an increase in biological activity. However the lack of an alkalinity to DOC correlation indicates that the variation in alkalinity is not highly dependent on biological activity. A substantial amount of the alkalinity increase in surface samples may be due to entrainment of higher alkalinity water from depth.

Sulfate ion concentrations increased throughout the summer. It is not possible to attribute the sulfate increases solely to either natural internal sources or atmospheric deposition. The internal sinks and sources of sulfate that operate on a seasonal basis tend to increase sulfate concentrations over the summer (Lazerte and Dillon 1984; Kelly, 1984). Rainfall concentrations of sulfate increase significantly throughout the summer in the Washington Cascades due to the more complete conversion and more effective washout of acid aerosols in summer rain (Logan et al., 1983) The August and September sampling trips followed rainfall events and [SO_4^{2-}] variation may in part reflect rainfall contributions. A change in concentration with depth is not well defined, suggesting that mixing and entrainment are not responsible for sulfate trends.

Welch et al. (1985) proposed using alkalinity/cation and alkalinity/conductivity ratios to indicate whether the lowered spring alkalinity was simply a dilution with low alkalinity snowmelt or was in part due to titration of alkalinity with acid (H_2SO_4). If alkalinity is not being replaced then these ratios will remain constant. If replacement is occurring due to snowmelt this should be reflected by lowered ratios in the

spring. These ratios remained constant for the study lakes and therefore do not indicate any bicarbonate replacement with sulfate. The range of both the alkalinity/cation (0.27-0.38) and alkalinity/conductivity (2.2-3.1) ratios found for the affected Alpine Wilderness Area lakes throughout the summer are significantly lower than those for temporally sampled lakes in this study (Alkalinity/ cation 0.92-0.91, alkalinity/cond 6.6-7.9). Approximately 80% of the stored acidic ions are released in the first 20% of snowmelt (Cadle et al., 1985). The resulting spike of acidification has been noted by many researchers (Klock and Lefohn, 1985; Welch et al., 1985). Since lake sampling in this study began after the initial spring snowmelt, the potential acid spike was probably not included in the sample data and it is therefore questionable whether the effect would have been detected.

5.3 Buffer System

In lakes dominated by the carbonate system, resistance to pH depression is achieved through the loss of alkalinity. For the range of pH values encountered in this study the maximum buffering capacity, as shown by the peak in Figure 9, occurs at pH = pK_{a1} of the carbonate system near pH = 6.4. The minimum buffering capacity occurs at the CO_2 equivalence point near pH = 5.25 for dilute systems. Therefore, systems at a pH near pKa_1 would require relatively much higher acid input, or would exhibit a much greater change in alkalinity, for a given change in pH than systems nearer the CO_2 equivalence point.

The similarity between the lake data and the theoretical curve with regard to equivalence points and slopes indicates the dominance of the carbonate buffer system in the lakes sampled. The pKa_1 value, or point of maximum buffer intensity, is sensitive to changes in ionic strength and

temperature. Although the pH value of the pKa_1 point does not change as a function of carbonate concentration, the magnitude of the buffering intensity does. In contrast, the buffer intensity minimum defined by the CO_2 equivalence point varies both in magnitude and pH value with changes in total carbonate concentration, or p_{CO_2}. This fact may explain the better theoretical fit at the maximum than at the minimum buffer intensity points. Lake pH values tend to stabilize where a buffering capacity is high rather than at minimum points, creating a bimodal distribution (Wright and Gjessing, 1976; Zimmerman, 1982). Zimmerman (1982) proposed that this distribution may be used to indicate acidification. Nonacidified areas would have lake pH values distributed around pK_{a1} (pH = 6.4). Acidified areas would show an increase in lake pH distribution where natural water or aluminum buffering potential increases, near pH = 5. Lakes in the transition zone (pH = 5.25-5.7) are characterized by severe pH fluctuations and are extremely sensitive to seasonal pulses of acid, as during snowmelt (Henricksen, 1980). Significant acidification has to occur before a bimodal distribution due to acidification is noticeable. Lakes would remain in the transition zone until almost all of the alkalinity is consumed (Henricksen, 1980). The acidified areas of the Adirondacks, when compared to historical data, have shown a definite shift to the acidified region of the bimodal distribution (Driscoll, 1985). The lakes in this study showed a pH distribution around the maximum buffer intensity (pK_{a1}) point (median pH = 6.4, Table 4), or nonacidified region.

The apparent lack of an additional weak buffering system indicates that equilibration at a higher p_{CO_2} is the best explanation for values falling above the theoretical pH vs. alkalinity line in Figures 3 and 4. The average p_{CO_2} as calculated from lab-equilibrated pH and alkalinity, was $10^{3.01}$

atm. This value is 3.1 times higher than the global average p_{CO_2} at sea level of $10^{-3.5}$ atm. Similar results were reported for the Central Washington Cascade lakes and Oregon Cascade lakes (Logan et al., 1983; Nelson and Delwiche, 1983). Logan et al., (1983) attributed the equilibration at a higher p_{CO_2} to temperature differences between lakes sampled and the laboratory. Nelson and Delwiche (1983) argued that since pH stabilizes asymptotically over long periods of time, the existence of a kinetic limitation on the equilibration of the water sample with atmospheric p_{CO_2} is indicated. Such a limitation may explain the apparent supersaturation caused by the higher soil p_{CO_2} relative to that of the atmosphere (Elzerman, 1983). The supersaturation illustrated in Figure 4 probably reflects this effect.

3.4 Aluminum Chemistry

The total aluminum concentrations determined in this study were similar to the total aluminum concentrations found by the U.S.G.S. (1986) study. Elevated levels of total aluminum are influenced by both organic and inorganic complexation and are not a response to acidification. Seasonal variation in total aluminum is a response to varying levels of organically complexed aluminum.

The general pattern of aluminum speciation observed in the study lakes agrees well with theoretical thermodynamic equilibrium models. The lake water data resembles aluminum trihydroxide equilibria and indicates that the relatively higher levels of aluminum found in some lakes is not associated with higher free ionic aluminum ($[Al^{3+}]$) concentrations or acidification. For the lakes studied, nearly all of the labile aluminum was theoretically predicted to be in the $Al(OH)_4^-$ form since the pH values were

generally above 6. Temporal changes in total aluminum concentration appear to be a function of changes in the organically complexed aluminum component which responded to changes in DOC.

Although dissolved organic carbon levels are low in the study lakes (mean DOC = 1.3 mg/L), the average organic aluminum/total aluminum ratio of 0.29 indicates that a significant amount of the aluminum is organically bound. The nonlabile or organically complexed aluminum is strongly correlated to DOC as seen by equation 42 (App. 2). Similar relationships have been found by other researchers (Wright, 1985; Driscoll, 1985; and Johnson, 1981). Levels of organic aluminum complexation are influenced by the altitude and position of the lakes in the watershed, the upper reaches containing less organically complexed aluminum.

Both the early summer and fall sampling trips occurred during runoff events of snowmelt or rainfall. Such events increase the levels of DOC and organically complexed aluminum in streamflows (Driscoll, 1984; Johnson et. al., 1984). It is likely that increased levels of aluminum in September are a response to inflow rather than to biogenically derived DOC. The one extreme total aluminum value of 80 ug/L for Tipsoo Lake is much lower than the average of 332 ug/L for three acidified Adirondack lakes (Driscoll, 1980). The mean total aluminum lake surface concentration of 11 ug/L is similar to the mean of 10 ug/L cited as background levels for natural water and less than the 16 ug/L for Oregon Cascade lakes (Stumm and Morgan, 1981; Nelson and Delwiche, 1983).

5.5 Sulfate

To relate sulfate concentrations to reduction in alkalinity or pH depression, Wright (1983) developed an "acidity index" equation based on

theoretical ion balance equations:

$$([H^+] - [HCO_3^-]) + 0.91\ ([Ca^{2+}] + [Mg^{2+}]) = [SO_4^{2-}]$$

An increase in $[SO_4^{2-}]$ through acid deposition causes either an increase in $([H^+] - [HCO^{-3}])$, which is equivalent to a decrease in alkalinity, an increase in $([Ca^{2+}] + [Mg^{2+}])$, or both.

Not all sulfate can be attributed to anthropogenic deposition. Concentrations of background sulfate, attributed in part to terrestrial dust, exist in pristine lakes (Wright, 1983). Background sulfate levels of 20 ueq/L and 15 ueq/L proposed by Galloway et al. (1983) and Wright and Henricksen (1983), respectively, and estimates from Wright's background (Bkg) sulfate equation;

$$\text{Bkg}\ [SO_4^{2-}] = 0.09\ ([Ca^{2+}]+[Mg^{2+}])+[Na^+]+[K^+]$$

are greater than those typically encountered in this study $\bar{X}$ = 80.4 ueq.

Estimates from an equation developed for this study using Wright's procedure

$$\text{Bkg}\ [SO_4^{2-}] = 7.1+0.05\ \Sigma\ [\text{cations}]$$

were similar to observed total $[SO_4^{2-}]$ (mean = 16.08 ueq/l, median = 12 ueq/L) suggesting levels at or near background levels.

Wright (1983) found net $[SO_4^{2-}]$ (total $[SO_4^{2-}]$ - Bkg $[SO_4^-]$) to be closely correlated ($r^2 = 0.99$) with alkalinity loss (Δ[Alk]) for North American lakes. Hendry and Brezonik (1983) and Zimmerman (1982), using similar indices (Net $[SO_4^{2-}]$ - [Alk], Net $[SO_4^{2-}]$/[Alk]), found a strong negative correlation with pH ($r^2 = 0.71$). These methods did not associate net $[SO_4^{2-}]$ with loss of alkalinity or pH depression in the lakes studied.

A number of researchers have documented the mitigating effects of

natural processes such as soil leaching and biochemical reduction on sulfate deposition. Correlating sulfate deposition rates to aquatic concentrations without an extensive mass balance analysis is, therefore, somewhat tenuous. Sulfate ion flux is increased by acidic deposition, resulting in an alkalinity decrease, and is consistent with the titration concept (Lazerte and Dillon, 1984).

The median lake surface [SO_4^{2-}] for the lakes studied of 8.3 ueq/L is at the low end of the 8.3 ueq/L to 14.8 ueq/L range in precipitation reported for Snoqualmie Pass, Washington (Logan et al., 1983). When high local sources of sulfate (Allen Lake) are not considered in this study, the average concentration (8.4 ueq/L) is greater than the average for the Oregon Cascade lakes (5.8 ueq/L) and less than the average for the Alpine Lakes Wilderness Area, Washington (13.1 ueq/L) (Nelson and Delwiche, 1983; Logan, 1985). Assuming similar base geology, the disparity in sulfate concentrations indicates that some sulfate in Washington is anthropogenically derived and that the effect is less important at Mount Rainier than in the Alpine Wilderness Area farther north. The level of acidification indicated by the disparity in sulfate data is below the resolution of the models used in this study to determine the extent of acidification (see section 5.6). The effect of sulfate deposition on lake water chemistry would be greatest during the initial snowmelt and could result in significant peaks of acidification in the extremely sensitive lakes (Table 5). Further study would be required to determine the presence and extent of the possible snowmelt induced pulse of acidification. The trend of increasing anthropogenic sulfate going north is consistent with prevailing weather patterns for Washington State.

5.6 Model Applications

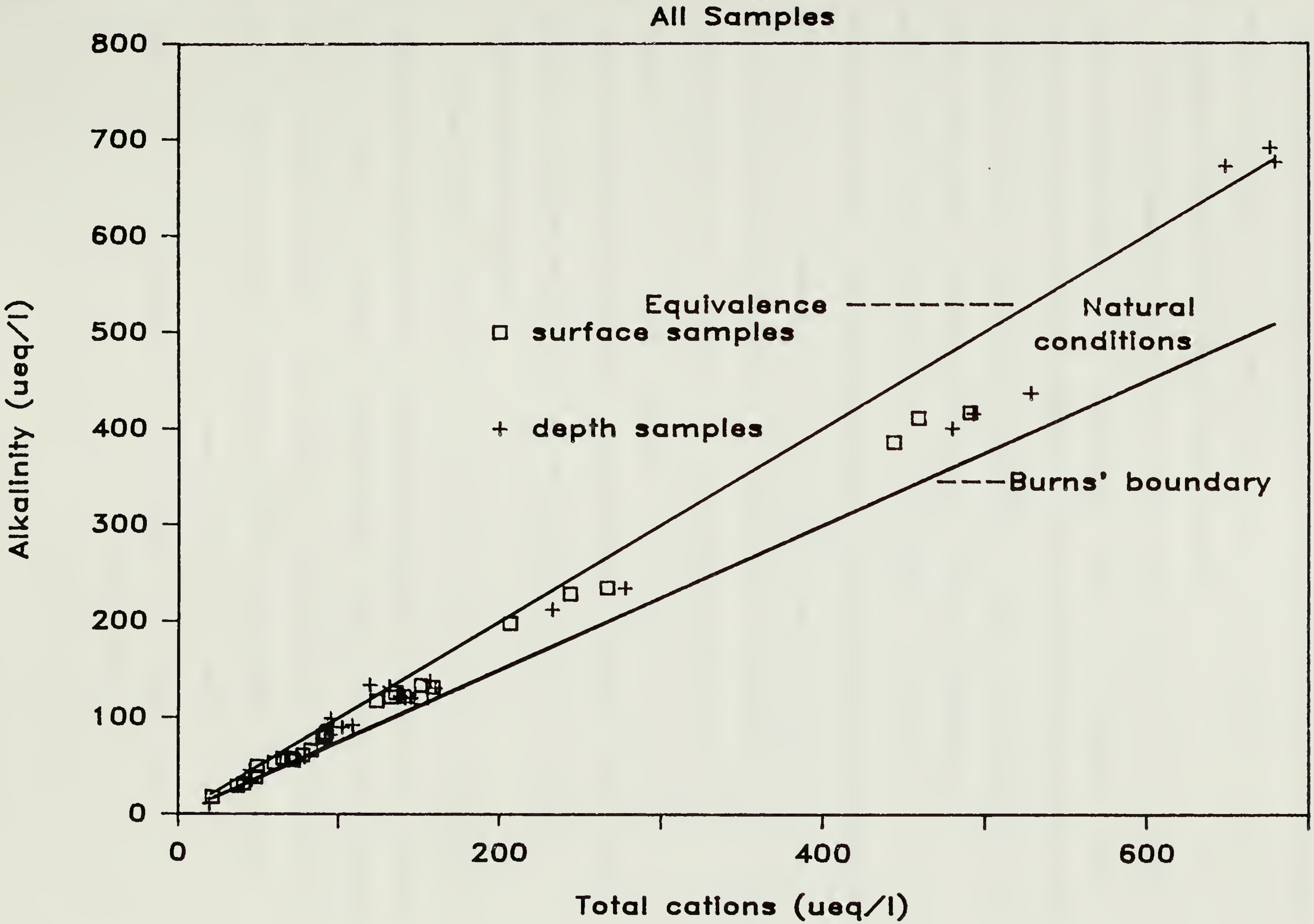
5.6.1 Electroneutrality

To determine the extent of acidification in the study lakes, water chemistry data is analyzed using models which are developed from equations presented in Table 1. The theoretical and empirical equations from Table 1 also provide a basis for comparing this studies data to that of other researchers.

By assuming carbonic acid weathering and fulfilling the requirements of electroneutrality, the correlation between alkalinity and total cations should result in a slope = 1 and y intercept = 0 (Eq. 7, Table 1). If strong mineral acid weathering has occurred in a given area, the slope will be less than one, indicating the release of cations without accompanying alkalinity, or the titration of bicarbonate. The closeness to theory of the alkalinity vs. cation equation (#34; [Alk] = -7.7 - 0.95 x [cations]; App. 2) indicates that carbonic acid weathering dominates the lake systems studied and that little, if any, acidification has occurred. A very similar equation ([Alk] = -8.66 + 1.05 x [cations]) was determined for the nonacidified Oregon Cascade lakes (Nelson and Delwiche, 1983).

Burns (1981) proposed an empirical method, based on the theoretically derived electroneutrality equation, by showing that in areas unaffected by acid deposition, the slope of the carbonic acid weathering line ([Alk] vs. [cations]) was greater than or equal to 0.75. A slope of one is seldom attained, which is attributed to either an alternative source of weak acid or the omission of a component anion (Burns, 1981; Zimmerman, 1982). The ratio for acidified areas was significantly lower, i.e., 0.064, Scandanavia; 0.185, Hubbard Brook, N.H.; and 0.562, North Carolina. Figure 11

Figure 11. Alkalinity vs. Total Cations



All Samples

illustrates Burns' model with the study lakes superimposed. The study lakes could lose an average of 11% of their bicarbonate alkalinity which is equal to an average of 13.7 ueq/L of acidification for surface samples, and not appear acidified according to Burns' method.

Only one sample, (Frozen lake, depth, August) falls below the empirical [Alk] vs. Σ[cations] ratio 0.75 defined by Burns as the boundary between natural conditions and acidification. This error may be due to the extreme diluteness of Frozen Lake (Zimmerman, 1982). However the ratio for Frozen lake surface sample lies above the limit. Since the lake was not stratified, the averaged values for the parameters were used which lie above the cutoff (0.75). The low dissolved silica and aluminum concentrations and the presence of a snowpack near the lake when sampled in August indicate that Frozen Lake receives most of its water from precipitation runoff rather than groundwater. The low pH (5.7) and extremely sensitive nature (conductivity = 3.5 umho/cm, alkalinity = 15.5 ueq/L) are within the expected range for precipitation dominated lakes (Klok and Lefohn, 1985). Therefore, by Burns method, none of the sampled lakes has received significant acid inputs.

To empirically determine if the key lakes "elevated" aluminum could be associated with low levels of acidification [Alk] vs. Σ [cation] equations were developed for both high aluminum (Golden, Mowich, Shriver) and typical aluminum (Mowich, Crystal, Allen) lakes. A higher level of acidification would result in a lowered intercept and slope in the [alk] vs. Σ[cation] correlation. The high aluminum lakes correlation's negative intercept and large slope (eq. 39) appear to be an artifact of the much higher ionic strength of the Golden Lake depth samples. When Golden Lake depth samples are omitted, the high aluminum (Eq. 40) and typical aluminum (Eq. 41)

equations are not significantly different ($p \leq 0.05$). Thus relatively high aluminum levels in the high aluminum lakes do not appear to be the result of acidification.

As discussed earlier the y-intercept of the electroneutrality equations (Eqs. 6 annitrogen-oxide-derived acidification (nitric acid) is unlikely to have occurred in the study area.

Models based on [Alk] vs. [Ca^{2+}] (Henricksen, 1979) and [Alk] vs. [Ca^{2+}] + [Mg^{2+}] (Henricksen, 1980) are essentially empirical simplifications of the theoretical electroneutrality equation (Eqs. 10, 11, Table 1). The empirical relationships derived from unacidified Norwegian lakes to describe original alkalinity underestimates observed nitrogen-oxide-derived acidification (nitric acid) is unlikely to have occurred in the study area.

Models based on [Alk] vs. [Ca^{2+}] (Henricksen, 1979) and [Alk] vs. [Ca^{2+}] + [Mg^{2+}] (Henricksen, 1980) are essentially empirical simplifications of the theoretical electroneutrality equation (Eqs. 10, 11, Table 1). The empirical relationships derived from unacidified Norwegian lakes to describe original alkalinity underestimates observed alkalinity in the Mt. Rainier study lakes by an average of 17% using the alkalinity vs. ([Ca^{2+}] + (Mg^{2+}] model and 23.8% using the alkalinity vs. [Ca^{2+}] model. Multiple regression indicates that this is due to the significant alkalinity associated with potassium and sodium. Welch and Chamberlain (1982) found that Henricksen's (1979) alkalinity vs. [Ca^{2+}] model underestimated observed alkalinity by 22% for Washington lakes in general.

5.6.2 Ion Concentration vs. pH Plots

Henricksen (1979) proposed a pH vs. [Ca^{2+}] equation to distinguish between acidified and nonacidified waters (e.g. 20, Table 1). The boundary

line ($[Ca^{2-}]$ vs. pH) between acidified and nonacidified lakes was empirically determined using data from 59 nonacidified Norwegian lakes (Henricksen, 1979). Figures 12 and 13 present Ca vs. pH data for the study lakes using lab-equilibrated and field pH values, respectively, and with Henricksen's boundary superimposed. Some loss of alkalinity, or a moderate drop in pH, could occur from acidification and most lakes would appear unimpacted according to Henricksen's model. Figure 14 compares the study lakes with the Washington Cascade lakes studied by Logan (1982).

Comparison of Figures 12 and 13 shows that selecting field pH over lab-equilibrated pH greatly increases the apparent level of acidification from the lakes studied. Being an intensity parameter, pH, when measured in the field, fluctuates significantly due to p_{CO_2} variation, photosynthesis, respiration, wave action, temperature, and measuring method. These factors are minimized by determining pH under consistent laboratory conditions. However, since no defined standard exists, it is difficult to compare pH data among investigators.

Kramer and Tessier (1982) suggest that plots of total cation concentration vs. pH provide a more suitable model for testing acidification since pH and alkalinity are directly related and the boundary line has theoretical justification, (Eq. 18, Table 1). Similar to previous methods this method indicated no acidification in the study lakes.

Figure 12. Calcium vs.Lab pH

All Samples

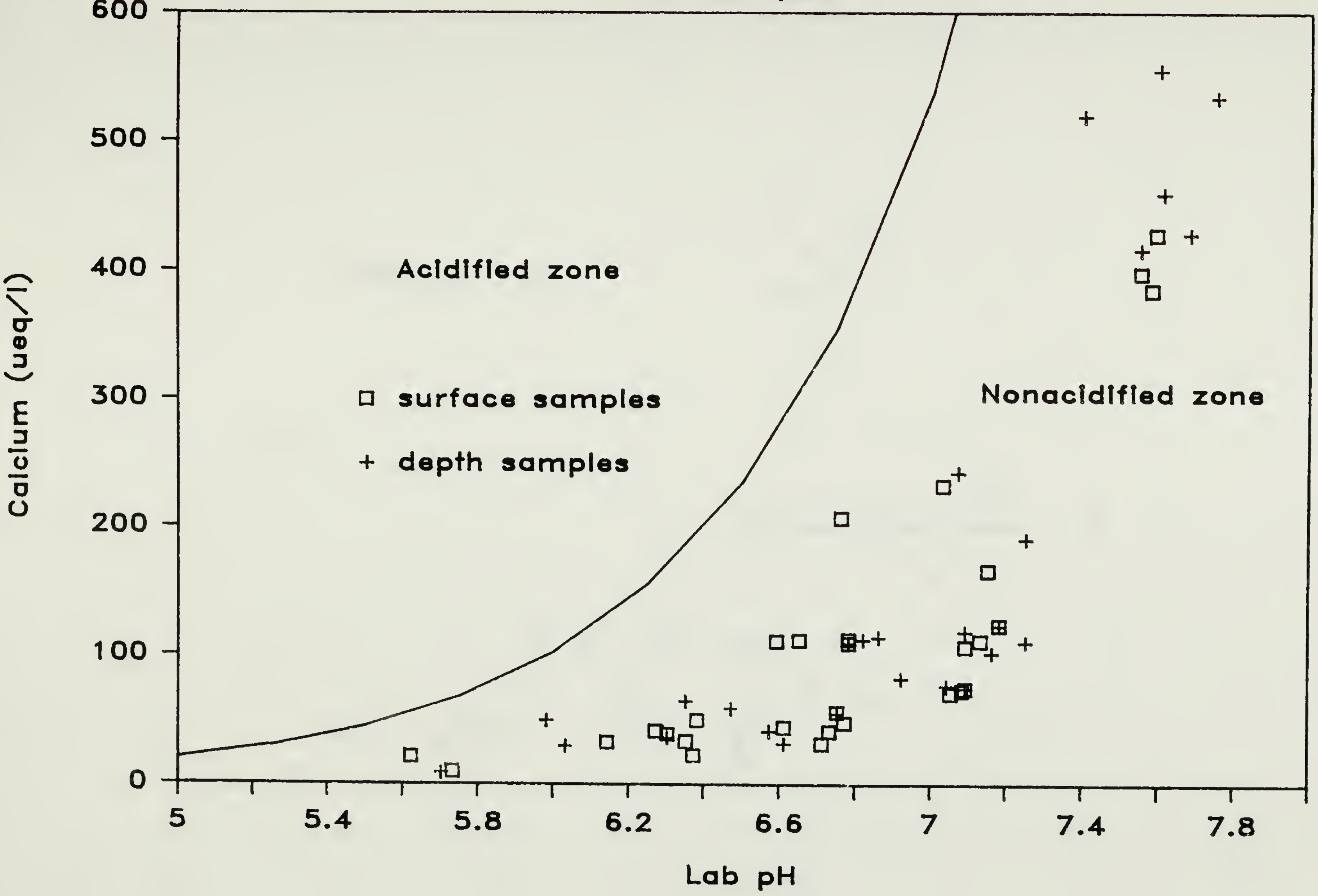


Figure 13. Calcium vs. Field pH

All Samples

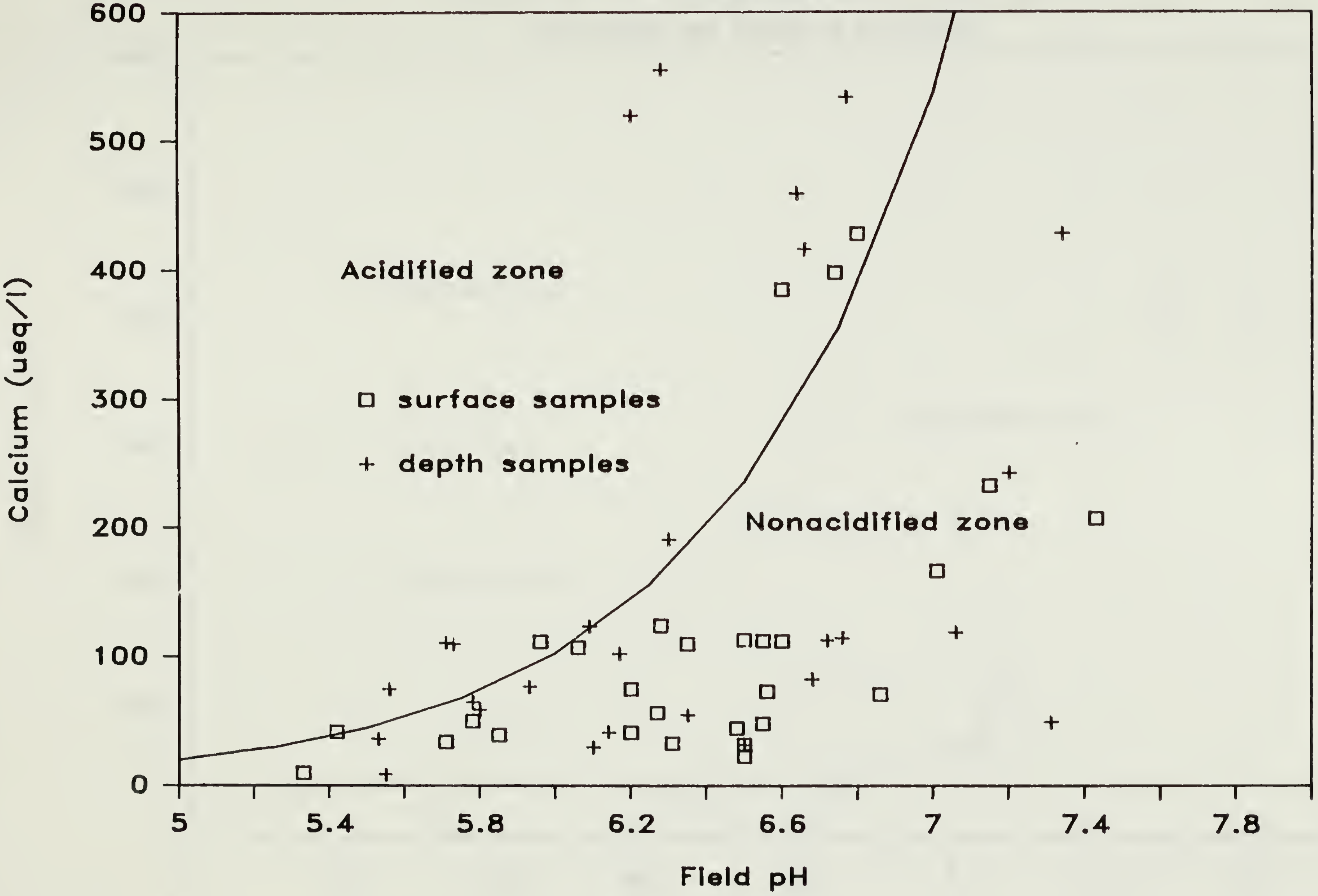
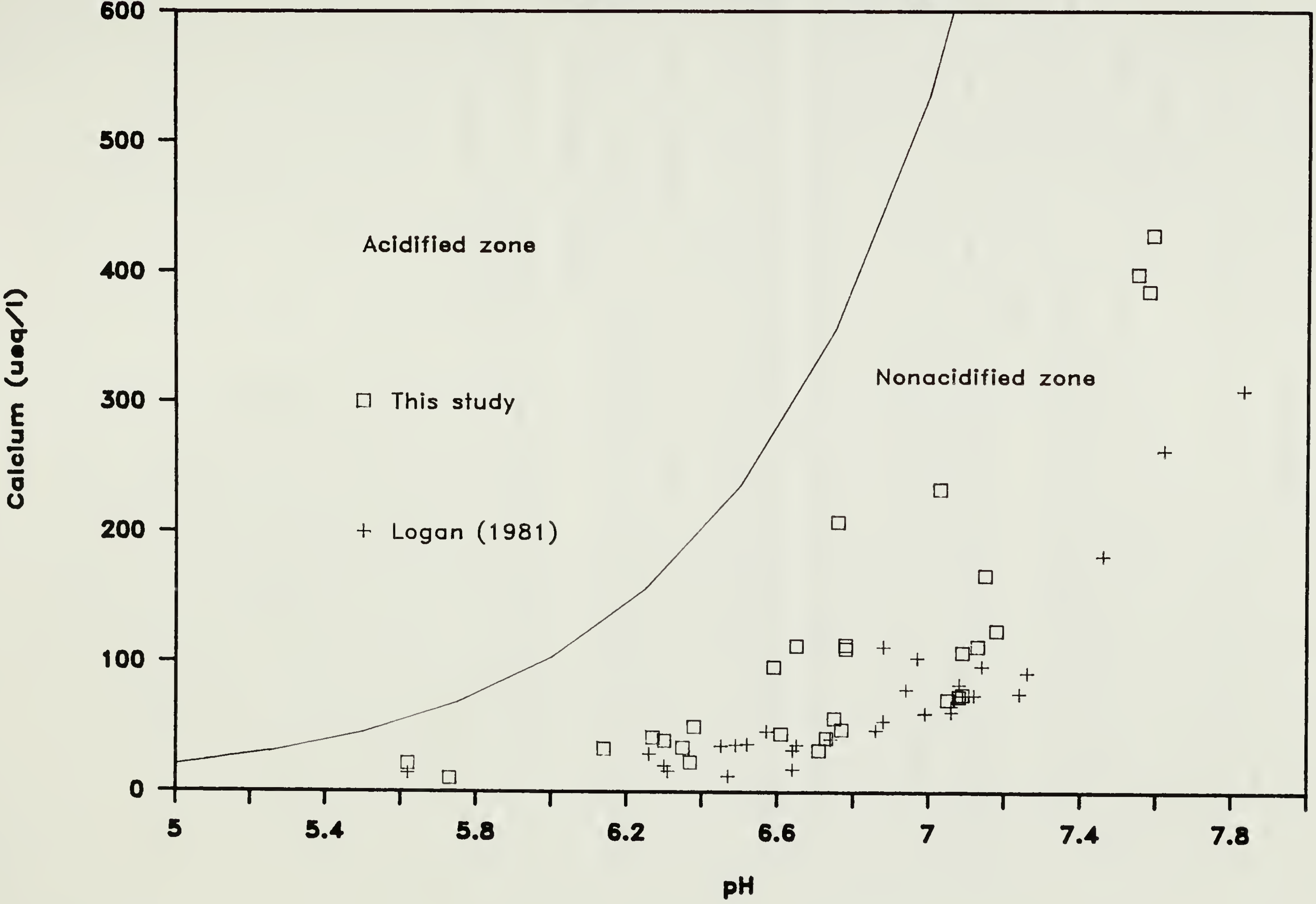


Figure 14. Calcium vs. pH

This Study and Logan et al. (1981)



6.0 CONCLUSIONS

With respect to the stated objectives, the following conclusions may be drawn from this study:

1) Mount Rainier National Park lakes are of a generally dilute ionic composition relative to average North American freshwater lakes but are typical of Cascade Mountain Lakes.

2) Most lakes in Mount Rainier National Park are highly susceptible to acidification from acid precipitation due to their diluteness and poor buffering capacity.

3) Observed dissolved aluminum concentrations simulate theoretical equilibrium with an aluminum trihydroxide phase similar to natural gibbsite The relatively higher concentrations of total aluminum observed in some lakes is not associated with the free aluminum ion cited as a symptom of acidification, but rather is attributable to natural soluble complexes with inorganic and organic ligands.

4) Based on ionic composition, Mount Rainier lakes exhibit no detectable level of acidification.

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Appendix 1

Lake Profiles
Mount Rainier National Park

Unnamed Lake

sample depth	DO profile Date sampled 7/3	8/12	9/22	Temperature profile Date sampled 7/3	8/12	9/22	depth
0.25	12	8.05	7.6	18.5	14.5	10.5	0.25
2.5	10.1	8.2	7.6	15.5	14.25	10.25	2.5
5	8.8	8.5	7.5	12.5	14	10.25	5
7.5	9.4	8.5	7.6	9.5	14	10.2	7.5
10	5.5	8	7.3	8	14	10.2	10
12.5	5.2	7.2	7.3	7	14	10.2	12.5
15	5	7	7.6	6.5	13	10.2	15
17.5	3.5	6.9	7.5	6.25	11	10.1	17.5
20	2.1	6.7	7.3	6	10.5	10.1	20
25	1.9	6	7.3	6	10	10.1	25
30	1.6	5.4	7.2	5.5	9.5	10	30
35	1.5	5.2	7.1	5.5	9	10	35
37	1.6	0.5	0.5	5.5	9	10	37

Crystal Lake

sample depth	DO profile date sampled 7/5	8/11	9/21	Temperature profile date sampled 7/5	8/11	9/21	depth
0.25	8.1	7.05	8.1	15.5	16.5	10.25	0.25
2.5	7.9	7.2	8.2	15.25	16.5	10	2.5
5	7.8	7.8	8.2	15.25	16.25	9.75	5
7.5	7.7	8.1	8	14.5	16	9.75	7.5
10	7.3	8.2	7.9	13.75	16	9.75	10
15	7.3	8	8	12	16	9.5	15
20	7.5	7.2	7.9	11.5	16	9.5	20
25	7.8	5	8	11.25	16	9.5	25
27.5	7.5	4.3	7.6	11.1	15.75	9.5	27.5
30	7.3	3.8	7.3	11	15.75	9.5	30

Allen Lake

	DO profile			Temperature profile			
sample	date sampled			date sampled			
depth	7/6	8/14	9/25	7/6	8/14	9/25	depth
0.25	8.5	7.8	7.8	15	17	12.[illegible]	0.25
2.5	8.9	7.75	7.8	12	16	11.75	2.5
5	11.4	7.6	7.7	9	15.75	10.5	5
7.5	8.5	7.8	7.8	6	15.5	10.25	7.5
10	5.8	7.6	7.7	7.25	15.5	10	10
12.5	4.7	7.9	7.8	7	15.25	10	12.5
15	4.35	7.9	8.2	6.5	15.25	10	15
17.5	4	7.7	8.2	6.5	15.25	10	17.5
20	4.2	n/a	n/a	6.25	n/a	n/a	20
24	3.5	n/a	n/a	6.25	n/a	n/a	24

Golden Lake

	DO profile			Temperature profile			temp pro
sample	date sampled			date sampled			
depth	7/9	8/15	9/25	7/9	8/15	9/25	depth
0.25	7.8	7.5	8.7	19.5	16.5	12	0.25
2.5	7.7	7.6	8.7	18.5	16.5	11	2.5
5	9.2	7.8	8.7	15	16	11	5
7.5	9.6	8	8.7	11.75	16	10.75	7.5
10	9	7.2	8.6	8.75	16	10.75	10
12.5	8.5	7.3	8.55	7.5	14	10.25	12.5
15	7.7	7	8.4	6.25	11.5	10	15
17.5	7.3	7.05	8.35	5.75	8.75	10	17.5
20	7.1	6.9	8.3	5.25	8	9.5	20
25	6.7	6.6	7.2	4.75	6.25	7.25	25
30	5.9	5.5	7.55	4.25	5.25	6	30
35	5	3.15	4.1	4.25	4.75	5.25	35
40	2.5	1.6	3.1	4.25	4.5	5	40
45	0.5	0.45	1.85	4	4.1	4.75	45
50	0.4	0.35	1.65	4	4	4.25	50

Mowich Lake

sample depth	DO profile date sampled 7/10	8/14	9/24	Temperature profile date sampled 7/10	8/14	9/24	depth
0.25	8.5	7.75	8.8	15.5	14	10	0.25
2.5	8.5	7.75	9	15.5	13.25	10	2.5
5	8.7	7.6	8.8	15	13	10	5
7.5	9.5	7.7	8.8	11.5	13	10	7.5
10	9.9	7.7	8.8	10	13	10	10
12.5	9.8	7.75	8.7	9	13	10	12.5
15	9.8	7.8	8.6	8	13	9.75	15
17.5	9.7	8	8.6	7.5	13	9.75	17.5
20	9.7	8.05	8.6	7	12.75	9.75	20
25	9.7	9	8.5	6.25	9.75	9.75	25
30	9.7	9.1	8.5	5.75	9	9.75	30
35	9.7	8.9	8.4	5.5	8	9.75	35
40	9.4	8.9	8.4	5	7.25	9.7	40
45	9.9	8.95	8.6	5	7	9.5	45
50	9.6	8.9	8.7	4.75	6.8	9	50

Shriner Lake

sample depth	DO profile dat 7/12	8/18	9/27	Temperature profile date sampled 7/12	8/18	9/27
0.25	7.4	6.7	8.7	21.75	20	12
2.5	7.3	6.9	8.8	21	19.75	12
5	7.2	6.7	8.7	20.75	19.75	11.5
7.5	7.5	6.5	8.6	20.5	19	11.25
10	7.7	6.6	8.5	20	19	11.5

George Lake

date 7/11

sample depth	Profiles DO	Temperature
0.25	8.4	16
2.5	8.8	16
5	9.1	14.75
7.5	9.4	12.75
10	9.6	11.75
12.5	9.5	10
15	9.5	10
20	8.8	8.25
25	8.6	7.5
30	8.3	6.5
35	8.4	6
40	8.2	5
45	7.8	5
50	7.6	4.75

Lake Louise

date sampled 7/4

sample depth	profiles DO	Temperature
0.25	9.6	9.25
2.5	10.25	8
5	10.4	8
7.5	10.5	7.5
10	11.2	7
15	11	7
20	10.6	6.5
25	10.2	6.5
30	9	6
35	8.4	5.75
40	8.1	5.25
45	7.2	5
50	6.5	5

Shadow Lake
date sampled 7/11

sample	profiles	
depth	DO	Temperature
0.25	8	18.5
2.5	8.2	17.25
5	8.3	16.75
7.5	8.3	16.25
10	8.6	15.25

Marsh Lake
date sampled 8/9

sample	profiles	
depth	DO	Temperature
0.25	7.2	16.25
2.5	7.2	16.25
5	7.2	16.25
7.5	7.3	16
10	7.1	16.25

Eunice Lake 8/14
date sampled 8/14

sample	profiles	
depth	DO	Temperature
0.25	7.9	14.5
2.5	7.85	14
5	8.1	13.5
7.5	8	13.5
10	8.2	13
12.5	8.3	13
15	8.2	13
20	8.25	12.5
25	8.7	11
30	9.4	10.75
35	9.5	10.5
40	9.3	10
45	9.3	9.75
50	8.8	9

Lake Eleanor
date sampled 9/23

sample	profiles	
depth	DO	Temperature
0.25	7.35	12.5
2.5	7.6	12
5	7.6	11.8
7.5	7.8	11.5
10	7.7	11.5
12.5	7.65	11.25
15	7.6	11.25
17.5	7.6	11.25
20	7.6	11.25
25	7.6	11.25
30	7.5	11.25
35	7.5	11.2
40	7.4	11.2

Reflection Lake
date sampled 9/22

sample	profiles	
depth	DO	Temperature
0.25	8.4	11
2.5	8.5	10.75
5	8.3	10.5
10	8.2	10
15	8.1	9.9
20	8.2	9.75
25	8.2	9.75

Frozen Lake
date sampled 8/19

sample	profiles	
depth	DO	Temperature
0.25	7.1	15.25
2.5	7.1	15
5	7.2	14
7.5	7.3	13.75
10	7.3	13.5
12.5	7.3	13.5
15	7.3	13.5
17.5	7.3	13.5
20	7.2	13.5

Tipsoo Lake
date s

sample	profiles	
depth	DO	Temperature
0.25	7.7	20
2.5	7.6	19
5	7.5	18
7.5	7.8	17.5

Appendix 2

Empirical Correlations of Selected Chemical Parameters Using Averaged Parameter Values, Sixteen Study Lakes, Mount Rainier National Park (Units are mole/l or equivalent/l unless otherwise noted.)

No.	Parameter (y)	Equation (b + mx)	r^2
1	pH Lab =	0.0 + 1.08 pH Field	0.54
2	log $[Ca^{2+}]$ =	-3.07 + 0.74 pH	0.81
3	log $[Mg^{2+}]$ =	-3.9 + 0.69 pH	0.74
4	log $[Na^{+}]$ =	-1.94 + 0.22 pH	0.31
5	log $[K^{+}]$ =	-2.73 + 0.46 pH	0.22
6	log [Cations] =	-2.12 + 0.62 pH	0.77
7	log $([Ca^{2+}]+[Mg^{2+}])$ =	-3.01 + 0.73 pH	0.80
8	log $[SO_4^{2-}]$ =	-2.46 + 0.50 pH	0.26
9	log $[F^{-}]$ =	-1.56 + 1.10 pH	0.06
10	log $[SiO_2]_{(mg/l)}$ =	0.24 + 0.14 pH	0.25
11	log $[HCO_3^{-}]$ =	-2.52 + 0.67 pH	0.78
11'	log $[HCO_3^{-}]$ =	0.69 + 0.18 pH Field	0.21
12	log $[Cl^{-}]$ =	-2.73 + 0.33 pH	0.22
13	log $DOC_{mg/l}$ =	-3.27 + 0.45 pH	0.20
14	log Cond =	-2.54 + 0.55 pH	0.71
14'	log Cond =	0.005 exp (1.19 pH)	0.73
15	$[Al]_{total}$ =	-100 + 17.9 pH	0.17
15'	$[Al]_{total}$ =	-148 + 25.1 pH Field	0.31
16	$[Al]_{organic}$ =	-2.75 + 0.8 pH	0.01
Conductivity			
17	$[Ca^{2+}]$ =	-25.5 + 7.43 Cond	0.99
18	$[Mg^{2+}]$ =	-2.04 + 0.52 Cond	0.93
9	$[Na^{+}]$ =	9.77 + 0.61 Cond	0.67
0	$[K^{+}]$ =	-0.22 + 0.11 Cond	0.43

21	[Cations] =	$-17.84 + 0.87$ Cond	0.99
22	$[SO_4^{2-}]$ =	$4.77 + 1.07$ Cond	0.46
23	$[Cl^-]_{mg/l}$ =	$8.52 + 0.15$ Cond	0.21
24	$[F^-]$ =	$0.55 + 0.11$ Cond	0.58
25	$[HCO_3^-]$ =	$-17.97 + 7.57$ Cond	0.99
26	$[Al]_{total\ ug/l}$ =	$-0.08 + 0.08$ Cond	0.29
27	$[SiO_2]$ =	$1.27 + 0.16$ Cond	0.57
28	Ionic strength =	$-3.09 + 1.44$ Cond	0.98

lkalinity

29	$[HCO_3^-]$ =	$5.24 + 1.09\ [Ca^{2+}]$	0.97
30	$[HCO_3^-]$ =	$16.13 + 14.91\ [Mg^{2+}]$	0.92
31	$[HCO_3^-]$ =	$-61.00 + 9.38\ [Na^+]$	0.73
32	$[HCO_3^-]$ =	$80.04 + 34.31\ [K^+]$	0.53
33	$[HCO_3^-]$ =	$5.25 + 1.02\ ([Ca^{2+}]+[Mg^{2+}])$	0.97
34	$[HCO_3^-]$ =	$-7.71 + 0.95$ [Cations]	0.99
35	$[HCO_3^-]$ =	$-184 + 22.75\ [SiO_2]_{mg/l}$	0.59
36	$[HCO_3^-]$ =	$104.5 + 34.80\ [Al]_{ug/l}$	0.35
37	$[HCO_3^-]$ =	$105.4 + 0.54$ DOC $_{mg/l}$	0.53
38	$[HCO_3^-]$ =	$-9.1 + 1.07$ [Cations]$-2[SO_4^{2-}]$	0.99
39	$[HCO_3^-]$ Test lakes =	$-20.88 + 1.05$ [Cations]	1.00
0	$[HCO_3^-]$ Test lakes (without Golden Lake depth sample)	$-0.5 + 0.85$ [Cations]	0.95
1	$[HCO_3^-]$ Control lakes	$13.01 + 0.82$ [Cations]	1.00
2	$[Al]_{organic\ ug/l}$ =	$2.58 + 4.15$ DOC$_{mg/l}$	0.80

ENRICKSEN'S EMPIRICAL EQUATIONS

3	[Alk] =	$-29 + 1.32\ [Ca^{2+}]$ (not seasalt corrected)
4	[Alk] =	$10 + 1.23\ [Ca^{2+}]$
5	[Alk] =	$0.0 + 1.21\ [Ca^{2+}]$
6	[Alk] =	$-14 + 0.91\ ([Ca^{2+}]+[Mg^{2+}])$

Appendix 3: Data Summary for Mt. Rainier Study

Table A3-1: Surface Samples

Lake	Trip	pH		Aluminum, ug/l		
		Field	Lab	Total	Organic	Labile
Golden	1	5.42	6.27	35.96	5.97	29.99
	2	6.48	6.61	21.17	4.23	16.93
	3	6.55	6.77	42.99	17.90	25.09
Mowich	1	6.86	7.05	2.74	0.41	2.33
	2	6.20	7.09	1.42	0.33	1.09
	3	6.56	7.08	6.39	0.26	6.13
Unnamed	1	5.85	6.30	1.14	0.51	0.63
	2	5.78	6.38	4.84	0.61	4.23
	3	6.27	6.75	4.83	2.10	2.73
Shriner	1	6.06	7.09	14.00	0.41	13.59
	2	6.28	7.18	16.51	0.32	16.19
	3	6.35	6.78	16.58	1.47	15.11
Crystal	1	5.96	6.59	1.57	0.30	1.27
	2	6.60	7.13	4.60	0.24	4.35
	3	6.55	6.65	9.38	5.57	3.80
Allen	1	6.60	7.58	2.37	1.28	1.08
	2	6.80	7.59	3.05	0.54	2.51
	3	6.74	7.55	4.94	3.46	1.48
Louise	1	6.50	6.37	1.73	0.50	1.23
Shadow	1	6.50	6.71	2.81	1.48	1.33
George	1	7.01	7.15	2.26	0.37	1.89
Marsh	2	6.31	6.14	2.83	1.38	1.45
Tipsoo	2	7.15	7.03	75.03	5.93	69.10
	3	7.43	6.76	81.03	10.77	70.26
Frozen	2	5.33	5.73	0.97	0.38	0.59
Eunice	2	5.71	6.35	4.00	1.10	2.90
Reflectio	3	6.20	6.73	6.41	4.01	2.40
Eleanor	3	6.50	6.78	5.15	1.24	3.91
Fan	3	N/A	5.62	7.67	4.01	3.66
max		7.43	7.59	81.03	17.90	70.26
min		0.00	5.62	0.97	0.24	0.59
avg		6.16	6.75	13.25	2.66	10.60
std		1.25	0.48	20.21	3.77	17.73

Lake	Trip	ANC		Anions, mg/l				
		ueq/l	mg/l as $CaCO_3$	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	F^-(ug/l)
Golden	1	57.57	2.88	0.00016	3.54	0.46	0.37	11.20
	2	58.06	2.90	0.00036	3.56	0.46	0.50	11.11
	3	61.20	3.06	0.00054	3.74	0.54	0.61	9.47
Mowich	1	79.16	3.96	0.00134	4.83	0.41	0.35	11.20
	2	84.53	4.23	0.00157	5.16	0.55	0.39	8.90
	3	81.81	4.09	0.00148	5.00	0.49	0.40	9.40
Unnamed	1	55.52	2.78	0.00017	3.42	0.46	0.50	13.27
	2	66.24	3.31	0.00024	4.07	0.43	0.57	14.96
	3	80.97	4.05	0.00069	4.95	0.51	0.65	10.85
Shriner	1	120.67	6.03	0.00223	7.37	0.27	0.69	15.75
	2	132.10	6.61	0.00301	8.06	0.33	0.97	16.30
	3	122.15	6.11	0.00111	7.46	0.42	0.95	16.16
Crystal	1	117.35	5.87	0.00069	7.17	0.10	0.18	13.27
	2	126.25	6.31	0.00256	7.71	0.07	0.20	14.33
	3	121.30	6.07	0.00082	7.41	0.17	0.25	12.31
Allen	1	336.73	19.34	0.02211	23.59	0.54	3.28	18.72
	2	418.06	20.90	0.02445	25.50	0.54	5.63	18.08
	3	411.71	20.59	0.02196	25.11	0.56	6.01	18.75
Louise	1	28.91	1.45	0.00010	1.79	0.35	0.10	8.71
Shadow	1	49.32	2.47	0.00038	3.02	0.10	0.15	17.75
George	1	198.07	9.90	0.00421	12.09	0.62	0.31	13.85
Marsh	2	53.06	2.65	0.00011	3.28	0.31	0.79	19.72
Tipsoo	2	234.72	11.74	0.00378	14.32	0.15	0.58	23.90
	3	228.44	11.42	0.00198	13.94	0.17	0.50	17.57
Frozen	2	17.45	0.87	0.00002	1.18	0.01	0.48	10.04
Eunice	2	38.14	1.91	0.00013	2.35	0.33	0.20	6.52
Reflection		57.91	2.90	0.00047	3.54	0.27	0.42	11.20
Eleanor	3	133.72	6.69	0.00121	8.17	0.50	1.87	20.27
Fan	3	31.25	1.56	0.00002	2.05	0.32	0.71	11.62
max		418.06	20.90	0.02445	25.50	0.62	6.01	23.90
min		17.45	0.87	0.00002	1.18	0.01	0.10	6.52
avg		125.94	6.30	0.00338	7.70	0.36	0.99	13.97
std		109.28	5.46	0.00671	6.65	0.17	1.45	4.12

		Cations, mg/l				
Lake	Trip	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SiO_2
Golden	1	0.85	0.12	0.61	0.06	4.16
	2	0.91	0.15	0.64	0.06	4.10
	3	0.98	0.18	0.74	0.07	4.25
Mowich	1	1.43	0.16	0.48	0.03	3.00
	2	1.52	0.17	0.47	0.04	2.93
	3	1.48	0.16	0.49	0.04	3.07
Unnamed	1	0.80	0.14	0.81	0.07	5.61
	2	1.02	0.17	0.79	0.05	5.59
	3	1.15	0.18	0.84	0.04	5.92
Shriner	1	2.16	0.26	0.79	0.22	3.51
	2	2.50	0.31	0.62	0.09	3.26
	3	2.22	0.29	0.62	0.05	2.25
Crystal	1	1.93	0.14	0.48	0.16	3.90
	2	2.25	0.14	0.42	0.06	3.47
	3	2.26	0.14	0.38	0.07	3.06
Allen	1	7.73	0.76	0.94	0.05	5.70
	2	8.59	0.86	0.93	0.09	4.23
	3	7.99	0.83	0.94	0.04	3.03
Louise	1	0.47	0.06	0.42	0.03	2.43
Shadow	1	0.65	0.11	0.32	0.06	3.64
George	1	3.36	0.32	0.85	0.13	4.00
Marsh	2	0.67	0.15	0.58	0.11	4.07
Tipsoo	2	4.67	0.23	0.61	0.09	2.35
	3	4.17	0.22	0.67	0.09	0.80
Frozen	2	0.20	0.02	0.24	0.02	3.29
Eunice	2	0.69	0.07	0.41	0.03	1.92
Reflection		0.84	0.16	0.53	0.03	3.80
Eleanor	3	2.28	0.43	0.73	0.03	4.58
Fan	3	0.44	0.09	0.47	0.08	3.15
max		8.59	0.86	0.94	0.22	5.92
min		0.20	0.02	0.24	0.02	0.80
avg		2.28	0.24	0.61	0.07	3.62
std		2.25	0.21	0.19	0.04	1.15

Lake	Trip	DOC mg/l	Cond. umho/cm	Calc. Ionic Str. mole/l	Total Cations ueq/l	Total Anions ueq/l	Ratio Tot.Cat. /An.
Golden	1	2.30	15.00	0.00011	79.87	78.96	1.01
	2	1.15	10.51	0.00012	86.74	82.01	1.06
	3	3.95	11.05	0.00013	96.39	89.46	1.08
Mowich	1	1.22	14.90	0.00015	105.26	98.56	1.07
	2	0.54	12.10	0.00016	110.49	108.49	1.02
	3	1.21	11.00	0.00015	108.11	104.51	1.03
Unnamed	1	0.53	12.90	0.00012	87.54	79.72	1.10
	2	0.54	12.10	0.00013	98.97	91.09	1.09
	3	0.87	10.60	0.00015	108.83	109.52	0.99
Shriner	1	0.67	19.10	0.00023	167.07	143.37	1.17
	2	1.32	16.80	0.00026	177.36	162.44	1.09
	3	1.51	18.90	0.00024	160.89	154.50	1.04
Crystal	1	1.36	17.30	0.00018	130.36	124.65	1.05
	2	1.24	18.05	0.00020	141.53	133.18	1.06
	3	1.28	15.00	0.00020	140.67	132.04	1.07
Allen	1	0.67	56.00	0.00074	483.53	471.22	1.03
	2	0.70	57.10	0.00086	534.24	551.26	0.97
	3	1.25	55.90	0.00083	501.87	553.69	0.91
Louise	1	0.55	5.95	0.00006	47.03	41.24	1.14
Shadow	1	0.96	7.10	0.00008	56.17	56.12	1.00
George	1	0.97	28.20	0.00033	231.51	222.68	1.04
Marsh	2	0.57	10.20	0.00011	72.50	79.15	0.92
Tipsoo	2	2.05	31.99	0.00040	276.17	252.28	1.09
	3	3.30	31.00	0.00037	253.39	244.66	1.04
Frozen	2	0.49	3.66	0.00004	22.41	28.32	0.79
Eunice	2	0.85	9.50	0.00008	58.06	51.96	1.12
Reflection		2.25	7.50	0.00011	78.40	74.79	1.05
Eleanor	3	0.73	18.38	0.00028	179.78	187.75	0.96
Fan	3	3.09	9.40	0.00008	51.21	55.59	0.92
max		3.95	57.10	0.00086	534.24	553.69	1.17
min		0.49	3.66	0.00004	22.41	28.32	0.79
avg		1.31	18.87	0.00024	160.23	157.35	1.03
std		0.88	14.36	0.00021	132.08	137.42	0.08

Lake	Trip	Ratio An/Cat	Ratio ANC/Cat	Ratio ANC/Cond
Golden	1	0.99	0.72	3.84
	2	0.95	0.67	5.52
	3	0.93	0.63	5.54
Mowich	1	0.94	0.75	5.31
	2	0.98	0.77	6.99
	3	0.97	0.76	7.44
Unnamed	1	0.91	0.63	4.30
	2	0.92	0.67	5.47
	3	1.01	0.74	7.64
Shriner	1	0.86	0.72	6.32
	2	0.92	0.74	7.86
	3	0.96	0.76	6.46
Crystal	1	0.96	0.90	6.78
	2	0.94	0.89	6.99
	3	0.94	0.86	8.09
Allen	1	0.97	0.80	6.91
	2	1.03	0.78	7.32
	3	1.10	0.82	7.37
Louise	1	0.88	0.61	4.86
Shadow	1	1.00	0.88	6.95
George	1	0.96	0.86	7.02
Marsh	2	1.09	0.73	5.20
Tipsoo	2	0.91	0.85	7.34
	3	0.96	0.90	7.37
Frozen	2	1.26	0.78	4.77
Eunice	2	0.90	0.66	4.02
Reflection		0.95	0.74	7.72
Eleanor	3	1.04	0.74	7.28
Fan	3	1.09	0.61	3.32
max		1.26	0.90	8.09
min		0.86	0.61	3.32
avg		0.98	0.76	6.28
std		0.08	0.09	1.33

Sea Salt Corr. Major Ion Conc., ueq/l

Lake	Trip	Ca^{2-}	Mg^{2+}	Na^{-}	K^{-}	SO_4^{2-}	HCO_3^{-}
Golden	1	41.84	2.79	19.07	1.37	4.09	58.09
	2	44.90	3.78	20.83	1.37	6.84	58.29
	3	48.20	4.40	23.68	1.48	8.38	61.36
Mowich	1	71.00	4.42	14.43	0.45	4.01	79.23
	2	75.33	4.28	11.91	0.71	3.74	84.60
	3	73.42	4.02	13.51	0.69	4.55	81.88
un-named	1	39.42	3.21	28.15	1.39	6.80	56.01
	2	50.31	4.38	27.35	1.05	8.43	66.64
	3	56.75	4.61	28.66	0.67	9.44	81.13
Shriner	1	107.46	8.38	29.99	5.57	12.13	120.73
	2	124.50	9.93	21.91	2.11	17.52	132.14
	3	110.10	9.14	20.32	0.96	16.50	122.29
Crystal	1	96.02	4.59	19.06	3.96	2.92	117.59
	2	112.35	4.71	17.30	1.39	3.65	126.30
	3	112.73	4.35	13.91	1.77	3.95	121.50
Allen	1	384.88	25.75	32.35	0.89	64.04	386.69
	2	428.14	29.12	31.93	1.99	112.94	418.00
	3	397.97	28.02	32.28	0.70	120.70	411.66
Louise	1	23.09	0.98	12.61	0.51	0.00	29.33
Shadow	1	32.13	3.66	12.35	1.37	2.25	40.51
George	1	166.92	9.50	27.08	2.97	1.60	198.10
Marsh	2	32.87	4.15	20.27	2.64	14.04	53.77
Tipsoo	2	232.90	7.63	23.98	2.21	10.81	234.77
	3	207.68	7.42	26.40	2.25	9.12	228.57
Frozen	2	10.12	0.69	10.11	0.54	9.98	19.31
Eunice	2	33.98	1.28	12.75	0.47	1.56	38.58
Reflection		41.59	4.92	18.82	0.66	6.66	58.08
Eleanor	3	113.31	13.71	23.98	0.48	34.87	133.86
Fan	3	21.67	1.90	15.60	1.79	12.28	33.65
max		428.14	29.12	32.35	5.57	120.70	418.00
min		10.12	0.69	10.11	0.45	0.00	19.31
avg		113.50	7.44	21.06	1.53	17.72	126.26
std		111.97	7.44	6.74	1.13	29.59	109.05

Ratios

Lake	Trip	HCO3/ Cat.	HCO3/ SO4	HCO / Cond.	SO4, Anal. /Sea	SO4 Bkg.	SO4 Bkg.	Tot.SO4 Sea+Bkg.
Golden	1	0.89	14.21	3.87	3.66	24.46	-16.71	-20.80
	2	0.82	8.53	5.55	3.62	26.58	-16.13	-22.96
	3	0.79	7.33	5.55	4.24	29.89	-17.27	-25.65
Mowich	1	0.88	19.77	5.32	3.24	21.67	-14.43	-18.43
	2	0.92	22.63	6.99	4.32	19.78	-11.72	-15.46
	3	0.89	18.00	7.44	3.86	21.17	-12.76	-17.31
Unnamed	1	0.78	8.24	4.34	3.65	33.38	-22.93	-29.73
	2	0.80	7.91	5.51	3.42	33.33	-21.48	-29.91
	3	0.89	8.60	7.65	4.06	34.85	-21.36	-30.80
Shriner	1	0.80	9.95	6.32	2.13	45.99	-31.73	-43.86
	2	0.83	7.54	7.87	2.62	36.12	-15.98	-33.50
	3	0.87	7.41	6.47	3.28	32.01	-12.23	-28.73
Crystal	1	0.95	40.25	6.80	0.81	32.07	-28.35	-31.27
	2	0.93	34.57	7.00	0.55	29.23	-25.02	-28.68
	3	0.92	30.74	8.10	1.34	26.21	-20.92	-24.87
Allen	1	0.87	6.04	6.91	4.26	70.19	-1.90	-65.94
	2	0.85	3.70	7.32	4.23	75.08	42.08	-70.85
	3	0.90	3.41	7.36	4.44	71.32	53.82	-66.80
Louise	1	0.79	N/A	4.93	2.08	15.29	-13.21	-13.21
Shadow	1	1.00	22.00	6.97	0.79	16.95	-13.91	-16.16
George	1	0.96	123.62	7.02	4.87	45.92	-39.45	-41.05
Marsh	2	0.90	3.83	5.27	2.41	26.24	-9.79	-23.83
Tipsoo	2	0.88	21.71	7.34	1.20	47.84	-35.82	-46.64
	3	0.94	25.06	7.37	1.35	48.01	-37.54	-46.66
Frozen	2	0.90	1.94	5.28	0.08	11.62	-1.57	-11.55
Eunice	2	0.80	24.77	4.06	2.61	16.39	-12.23	-13.79
Reflection	3	0.88	8.72	7.74	2.11	23.67	-14.91	-21.56
Eleanor	3	0.88	3.84	7.28	3.96	35.89	2.94	-31.93
Fan	3	0.82	2.74	3.58	2.50	19.51	-1.73	-17.01
max		1.00	123.62	8.10	4.87	75.08	53.82	-11.55
min		0.78	0.00	3.58	0.08	11.62	-39.45	-70.85
avg		0.87	17.14	6.32	2.82	33.47	-12.94	-30.66
std		0.06	22.64	1.28	1.33	16.26	19.48	15.80

Table A3-2:

		pH		Aluminum, ug/l		
Lake	Trip	Field	Lab	Total	Organic	Labile
Golden	1	6.77	7.75	90.00	NA	NA
	2	6.20	7.40	88.72	NA	NA
	3	6.28	7.60	89.00	NA	NA
Mowich	1	5.93	7.04	2.66	NA	NA
	2	5.56	7.09	0.79	NA	NA
	3	6.68	6.92	2.01	NA	NA
Unnamed	1	5.80	6.47	1.14	NA	NA
	2	5.78	6.35	2.39	NA	NA
	3	6.35	6.75	4.51	NA	NA
Shriner	1	6.17	7.16	14.00	NA	NA
	2	6.09	7.18	12.45	NA	NA
	3	5.73	6.78	14.47	NA	NA
Crystal	1	5.71	7.25	1.08	NA	NA
	2	6.76	6.86	4.01	NA	NA
	3	6.72	6.82	10.70	NA	NA
Allen	1	6.64	7.61	2.37	NA	NA
	2	7.34	7.68	3.01	NA	NA
	3	6.66	7.55	4.31	NA	NA
Louise	1	6.10	6.03	2.45	NA	NA
Shadow	1	6.50	6.61	2.81	NA	NA
George	1	6.30	7.25	0.89	NA	NA
Marsh	2	7.31	5.98	3.29	NA	NA
Tipsoo	2	7.20	7.07	78.47	NA	NA
Frozen	2	5.55	5.70	0.83	NA	NA
Eunice	2	5.53	6.30	1.83	NA	NA
Reflectio	3	6.14	6.57	6.26	NA	NA
Eleanor	3	7.06	7.09	2.19	NA	NA
max		7.34	7.75	90.00	NA	NA
min		5.53	5.70	0.79	NA	NA
avg		6.33	6.92	16.56	NA	NA
std		0.53	0.53	29.49	NA	NA
Surface - Depth						
max		7.43	7.75	90.00	17.90	70.26
min		0.00	0.00	0.00	0.00	0.00
avg		5.78	6.50	15.03	2.99	11.95
std		1.88	1.52	25.43	4.39	19.46

Lake	Trip	ANC ueq/l	ANC mg/l as $CaCO_3$	Anions, mg/l CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	F^-(ug/l)
Golden	1	680.00	34.00	0.05749	41.48	0.51	0.90	37.99
	2	673.20	33.66	0.02543	41.07	0.89	2.83	26.80
	3	693.50	34.68	0.04151	42.30	1.12	1.06	24.52
Mowich	1	81.69	4.08	0.00135	4.99	0.59	0.31	11.20
	2	93.65	4.68	0.00173	5.72	0.55	0.46	10.04
	3	90.10	4.51	0.00113	5.50	0.51	0.49	10.39
Unnamed	1	99.60	4.98	0.00044	6.10	0.57	0.31	15.75
	2	92.20	4.61	0.00031	5.65	0.46	0.46	14.33
	3	86.98	4.35	0.00074	5.32	0.53	0.65	11.77
Shriner	1	120.68	6.03	0.00262	7.37	0.27	0.68	15.75
	2	131.38	6.57	0.00299	8.02	0.24	0.96	15.89
	3	120.70	6.04	0.00109	7.37	0.42	0.91	18.87
Crystal	1	134.60	6.73	0.00360	8.21	1.07	0.20	13.27
	2	122.30	6.12	0.00133	7.47	0.10	0.22	15.88
	3	132.50	6.63	0.00132	8.09	0.22	0.26	13.69
Allen	1	438.42	21.92	0.02685	26.74	0.51	4.06	20.42
	2	416.70	20.84	0.02999	25.42	0.59	6.03	17.93
	3	400.94	20.05	0.02139	24.46	0.56	6.17	20.66
Louise	1	35.40	1.77	0.00006	2.22	0.41	0.20	10.29
Shadow	1	45.80	2.29	0.00028	2.81	0.37	0.30	15.75
George	1	213.00	10.65	0.00570	13.00	0.62	0.85	13.85
Marsh	2	58.95	2.95	0.00009	3.66	0.28	0.87	20.25
Tipsoo	2	235.00	11.75	0.00415	14.34	0.15	0.59	24.98
Frozen	2	10.30	0.52	0.00001	0.75	0.05	0.29	9.96
Eunice	2	35.46	1.77	0.00011	2.19	0.66	0.20	6.79
Reflection		62.00	3.10	0.00035	3.80	0.27	0.43	11.20
Eleanor	3	138.60	6.93	0.00257	8.46	0.61	1.87	19.88
max		693.50	34.68	0.05749	42.30	1.12	6.17	37.99
min		10.30	0.52	0.00001	0.75	0.05	0.20	6.79
avg		201.62	10.08	0.00869	12.31	0.49	1.21	16.60
std		202.21	10.11	0.01467	12.32	0.25	1.62	6.48
max		693.50	34.68	0.05749	42.30	1.12	6.17	37.99
min		0.00	0.00	0.00000	0.00	0.00	0.00	0.00
avg		155.03	7.63	0.00574	9.33	0.40	1.11	14.54
std		164.11	8.20	0.01121	9.99	0.23	1.60	6.27

Cations, mg/l

Lake	Trip	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SiO_2
Golden	1	10.72	1.17	2.24	0.58	18.57
	2	10.43	1.09	2.04	0.71	19.11
	3	11.16	1.13	1.95	0.68	19.11
Mowich	1	1.56	0.19	0.51	0.03	2.96
	2	1.52	0.18	0.48	0.06	3.09
	3	1.68	0.19	0.50	0.03	3.30
Unnamed	1	1.20	0.23	0.85	0.10	7.73
	2	1.32	0.23	0.93	0.16	6.65
	3	1.11	0.20	0.85	0.12	5.98
Shriner	1	2.07	0.26	0.79	0.16	3.70
	2	2.49	0.33	0.62	0.08	3.16
	3	2.22	0.32	0.62	0.05	2.25
Crystal	1	2.26	0.16	0.48	0.13	3.66
	2	2.30	0.15	0.43	0.06	3.55
	3	2.27	0.15	0.38	0.05	3.29
Allen	1	9.22	0.98	0.97	0.05	6.25
	2	8.59	0.93	0.93	0.08	3.32
	3	8.35	0.88	0.96	0.05	3.08
Louise	1	0.60	0.07	0.47	0.04	2.65
Shadow	1	0.64	0.13	0.32	0.08	3.74
George	1	3.86	0.35	0.86	0.13	4.24
Marsh	2	1.00	0.19	0.58	0.10	4.20
Tipsoo	2	4.88	0.23	0.60	0.12	2.33
Frozen	2	0.17	0.03	0.24	0.04	3.36
Eunice	2	0.75	0.07	0.44	0.03	1.64
Reflection		0.85	0.19	0.55	0.04	3.80
Eleanor	3	2.41	0.48	0.73	0.02	4.69
max		11.16	1.17	2.24	0.71	19.11
min		0.17	0.03	0.24	0.02	1.64
avg		3.54	0.39	0.79	0.14	5.53
std		3.49	0.36	0.50	0.19	4.93
max		11.16	1.17	2.24	0.71	19.11
min		0.00	0.00	0.00	0.00	0.00
avg		2.78	0.30	0.66	0.10	4.29
std		2.99	0.30	0.39	0.13	3.61

Lake	Trip	DOC mg/l	Cond. umho/cm	Calc. Ionic Str. mole/l	Total Cations ueq/l	Total Anions ueq/l	Ratio Tot.Cat. /An.
Golden	1	20.63	83.00	0.00106	734.01	715.02	1.03
	2	22.31	77.50	0.00107	708.32	758.69	0.93
	3	24.77	75.05	0.00109	741.76	748.49	0.99
Mowich	1	1.20	16.50	0.00016.	115.07	105.49	1.09
	2	0.50	11.90	0.00017	112.13	119.14	0.94
	3	1.20	12.50	0.00017	120.68	115.32	1.05
Unnamed	1	0.25	15.20	0.00016	116.79	122.94	0.95
	2	0.30	13.00	0.00017	127.82	115.47	1.11
	3	0.28	10.60	0.00016	111.27	115.98	0.96
Shriner	1	0.97	18.90	0.00022	161.10	143.36	1.12
	2	1.30	16.80	0.00026	177.82	159.03	1.12
	3	1.50	19.10	0.00024	162.81	152.37	1.07
Crystal	1	0.90	19.00	0.00022	147.69	169.65	0.87
	2	1.20	18.70	0.00020	145.20	130.59	1.11
	3	1.30	13.50	0.00021	141.21	144.85	0.97
Allen	1	0.73	65.10	0.00087	576.02	538.53	1.07
	2	0.75	57.10	0.00087	540.68	559.64	0.97
	3	0.75	55.00	0.00085	524.72	546.36	0.96
Louise	1	0.45	7.50	0.00007	56.53	51.70	1.09
Shadow	1	1.50	11.00	0.00009	57.93	63.34	0.91
George	1	0.83	29.00	0.00038	258.59	248.83	1.04
Marsh	2	0.26	10.40	0.00013	92.64	86.04	1.08
Tipsoo	2	3.00	32.00	0.00041	287.37	252.87	1.14
Frozen	2	0.23	3.47	0.00003	21.87	18.30	1.20
Eunice	2	0.01	9.20	0.00008	62.24	58.60	1.06
Reflection		2.20	7.35	0.00011	81.72	79.14	1.03
Eleanor	3	0.67	19.20	0.00029	189.77	195.72	0.97
max		24.77	83.00	0.00109	741.76	758.69	1.20
min		0.01	3.47	0.00003	21.87	18.30	0.87
avg		3.33	26.95	0.00036	243.47	241.31	1.03
std		6.85	23.64	0.00034	222.02	226.18	0.08
Surface + Depth							
max		24.77	83.00	0.00109	741.76	758.69	1.20
min		0.00	0.00	0.00000	0.00	0.00	0.00
avg		2.17	22.08	0.00028	191.58	189.77	0.96
std		4.69	19.93	0.00029	186.82	191.13	0.26

Lake	Trip	Ratio An/Cat	Ratio ANC/Cat	Ratio ANC/Cond
Golden	1	0.97	0.93	8.19
	2	1.07	0.95	8.69
	3	1.01	0.93	9.24
Mowich	1	0.92	0.71	4.95
	2	1.06	0.84	7.87
	3	0.96	0.75	7.21
Unnamed	1	1.05	0.85	6.55
	2	0.90	0.72	7.09
	3	1.04	0.78	8.21
Shriner	1	0.89	0.75	6.38
	2	0.89	0.74	7.82
	3	0.94	0.74	6.32
Crystal	1	1.15	0.91	7.08
	2	0.90	0.84	6.54
	3	1.03	0.94	9.81
Allen	1	0.93	0.76	6.73
	2	1.04	0.77	7.30
	3	1.04	0.76	7.29
Louise	1	0.91	0.63	4.72
Shadow	1	1.09	0.79	4.16
George	1	0.96	0.82	7.34
Marsh	2	0.93	0.64	5.67
Tipsoo	2	0.88	0.82	7.34
Frozen	2	0.84	0.47	2.97
Eunice	2	0.94	0.57	3.85
Reflection		0.97	0.76	8.44
Eleanor	3	1.03	0.73	7.22
max		1.15	0.95	9.81
min		0.84	0.47	2.97
avg		0.98	0.77	6.85
std		0.08	0.11	1.60
Surface + Depth				
max		1.26	0.95	9.81
min		0.00	0.00	0.00
avg		0.92	0.72	6.13
std		0.25	0.21	2.12

Sea Salt Corr. Major Ion Conc., ueq/l

Lake	Trip	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	HCO_3^{-}
Golden	1	534.11	40.59	89.61	14.61	14.61	679.90
	2	519.40	36.51	74.65	17.62	51.96	673.12
	3	555.23	36.76	67.14	16.66	13.08	693.40
Mowich	1	77.01	4.68	12.88	0.50	1.87	81.77
	2	75.27	4.57	12.38	1.18	5.21	93.71
	3	83.06	5.07	13.83	0.37	6.15	90.20
Unnamed	1	58.91	6.05	28.00	2.27	1.85	99.92
	2	65.14	6.50	33.42	3.73	5.96	92.63
	3	54.79	5.43	28.63	2.77	9.38	87.14
Shriner	1	102.93	8.43	29.91	3.88	12.00	120.72
	2	123.99	10.96	22.96	1.96	18.08	131.42
	3	110.02	9.94	20.32	1.07	15.66	120.84
Crystal	1	111.19	1.70	3.89	2.75	0.00	134.63
	2	114.84	4.97	17.06	1.44	3.78	122.42
	3	112.99	4.52	13.00	1.23	3.69	132.63
Allen	1	459.49	33.64	34.04	1.09	80.47	438.37
	2	427.96	31.73	31.44	1.78	120.84	416.65
	3	416.10	29.87	32.79	0.94	124.03	400.90
Louise	1	29.61	0.89	13.82	0.85	0.92	36.32
Shadow	1	31.52	3.26	8.10	1.78	3.32	46.04
George	1	191.58	10.49	27.58	2.96	12.83	213.02
Marsh	2	49.65	5.77	21.03	2.46	15.90	59.99
Tipsoo	2	243.14	7.87	23.68	3.05	11.03	235.04
Frozen	2	8.65	0.74	9.43	0.94	5.64	12.29
Eunice	2	36.60	0.00	8.83	0.29	0.00	35.96
Reflection		41.87	5.82	19.52	0.89	6.83	62.26
Eleanor	3	119.23	15.10	22.31	0.21	34.00	138.66
max		555.23	40.59	89.61	17.62	124.03	693.40
min		8.65	0.00	3.89	0.21	0.00	12.29
avg		176.08	12.29	26.68	3.31	21.45	201.85
std		173.92	12.59	19.93	4.72	33.25	202.00
Surface + Depth							
max		555.23	40.59	89.61	17.62	124.03	693.40
min		0.00	0.00	0.00	0.00	0.00	0.00
avg		136.09	9.55	22.60	2.30	20.01	155.31
std		148.67	10.52	15.07	3.38	32.68	163.90

Lake	Trip	Ratios HCO3/ Cat.	HCO3/ SO4	HCO / Cond.	SO4, Anal. /Sea	SO4 Bkg.	SO4 Bkg.	Tot.SO4 Sea+Bkg.
Golden	1	1.00	46.55	8.19	4.03	155.95	-137.31	-151.92
	2	1.04	12.95	8.69	7.03	142.30	-83.32	-135.28
	3	1.03	53.00	9.24	8.88	137.08	-115.11	-128.19
Mowich	1	0.86	43.72	4.96	4.67	20.73	-14.20	-16.07
	2	1.00	18.00	7.88	4.32	20.74	-11.21	-16.42
	3	0.88	14.67	7.22	4.05	22.13	-11.93	-18.08
Unnamed	1	1.05	53.90	6.57	4.52	36.12	-29.75	-31.60
	2	0.85	15.55	7.13	3.62	43.60	-34.02	-39.98
	3	0.95	9.29	8.22	4.16	36.82	-23.28	-32.66
Shriner	1	0.83	10.06	6.39	2.16	43.81	-29.65	-41.66
	2	0.82	7.27	7.82	1.91	37.06	-17.07	-35.15
	3	0.85	7.71	6.33	3.28	32.19	-13.24	-28.90
Crystal	1	1.13	N/A	7.09	4.16	16.80	-12.64	-12.64
	2	0.89	32.43	6.55	0.81	29.28	-24.70	-28.47
	3	1.01	35.98	9.82	1.74	24.81	-19.39	-23.08
Allen	1	0.83	5.45	6.73	4.06	79.52	5.01	-75.46
	2	0.85	3.45	7.30	4.63	74.59	50.87	-69.97
	3	0.84	3.23	7.29	4.44	73.86	54.61	-69.42
Louise	1	0.80	39.56	4.84	3.25	17.42	-13.26	-14.18
Shadow	1	1.03	13.88	4.19	2.93	13.01	-6.76	-10.08
George	1	0.92	16.61	7.35	4.87	48.73	-31.03	-43.86
Marsh	2	0.76	3.77	5.77	2.21	28.47	-10.36	-26.26
Tipsoo	2	0.85	21.30	7.35	1.21	49.32	-37.08	-48.11
Frozen	2	0.62	2.18	3.54	0.40	11.21	-5.18	-10.81
Eunice	2	0.79	N/A	3.91	4.16	12.41	-8.25	-8.25
Reflection		0.91	9.11	8.47	2.12	24.70	-15.74	-22.58
Eleanor	3	0.88	4.08	7.22	4.83	34.61	4.22	-29.78
max		1.13	53.90	9.82	8.88	155.95	54.61	-8.25
min		0.62	0.00	3.54	0.40	11.21	-137.31	-151.92
avg		0.90	17.91	6.89	3.65	46.94	-21.84	-43.29
std		0.11	16.53	1.54	1.78	39.16	38.65	38.13
Surface + Depth								
max		1.13	123.62	9.82	8.88	155.95	54.61	15.80
min		0.00	0.00	0.00	0.00	0.00	-137.31	-151.92
avg		0.83	18.45	6.17	3.00	38.92	-15.23	-34.76
std		0.23	23.56	2.09	1.74	30.24	31.03	30.00

Appendix 4

Nomenclature

p_{CO_2} : Partial pressure of atmospheric CO_2

$[i]$: Molar concentration of any species, i

Σ[cations] : equivalent sum of major cations

$= (2[Ca^{2+}]+2[Mg^{2+}]+[Na^+]+[K^+])$

D.O. : Dissolved oxygen

pH : Negative log $[H^+]$

$[ANC]_{f=0}$.carbonate : Acid neutralizing capacity, equivalents of acid required to titrate a water to the H_2CO_3 equivalence point (f=0) for the carbonate system; equal to [Alkalinity] for carbonate buffered waters

where $[Alkalinity] = [HCO_3^-]+2[CO_3^{2-}]+[OH^-]-[H^+]$
$\cong [HCO_3^-]$ for pH range 5.5 to 9.5

K_{a_1} : First acid dissociation constant, carbonate system

K_H : Henry's Law constant for $CO_2(g)$ solubility in water

$^*K$: Composite first acid dissociation constant, carbonate system $= K_{a_1} K_H$

K_a,org : Acid dissociation constant for model organic acid

K_{so} : Solubility constant for solid phase dissociation

pK_{so} : Negative log of solubility constant

Δ : Change in (loss of)

r^2 : Correlation coefficient squared (coefficient of determination)

α : Empirical constant equaling $= \log b' - \log {}^*K_{a_1} - \log p_{CO_2}$

b, b' : Empirical constants